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Atmospheric Transport and Deposition of Polychlorinated Dibenzo-'P'-Dioxins and Dibenzofurans

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ATMOSPHERIC TRANSPORT AND DEPOSITION OF POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are toxic compounds which are dispersed through the environment by atmospheric transport and deposition. It has been previously shown that there is a varying mixture of these compounds produced by combustion (the source of these compounds). Conversely, sedimentary sinks have been shown to have a constant sample pattern. Therefore, the goal of this project was to study PCDD/F in ambient air and rain samples (the transport media linking source to sink) in an effort to enhance our understanding of the physical/chemical parameters controlling the transformations which take place during atmospheric transport and deposition.

Analytical methods included high-volume air sampling, wet-only rain sampling, column chromatographic cleanup, and an electron capture, negative ionization form of gas chromatographic mass spectrometry. Air and rain samples were divided into vapor-phase and particle-bound or dissolved and particle-bound fractions, respectively.

The results showed that total concentrations in Bloomington, Indiana, had a geometric standard deviation range from 1.4 to 4.4 pg/m^3 in air and from 63 to 220 pg/L in rainwater. The vapor-to-particle (V/P) ratio for individual congeners ranged from 0.01 to 30. This ratio is controlled by the individual congener's vapor pressure and ambient temperature. Heats of adsorption were estimated from V/P *versus* 1/T regressions and ranged from -10 to -32 kcal/mole. Subcooled-liquid vapor pressures of PCDD/F congeners with 4 to 8 chlorine atoms were measured and shown to range from 10^{-6} to 10^{-9} torr.

Estimates of washout and the Henry's law constants were obtained using average ambient air and rain data. Total washout ranged from 10,000 to 90,000 for the tetra- through octa- homologues; Henry's law constants ranged from 1.3×10^{-5} to 8.9×10^{-8} atm$\cdot$ m^3/mole.

Atmospheric concentrations were shown to be consistent with previously observed sediment fluxes. Principal component analysis was used to compare the observed air and rain data with literature data for sources and sinks. This analysis indicates that the observed homologue profiles bridge the gap between source and sink profiles. The underlying characteristics of individual PCDD/F congeners (such as vapor pressure and Henry's law constant) show trends with level of chlorination. When transport and depositional processes act on those trends, the varying mixture in the sources becomes the consistent pattern in the sinks.

This report is submitted in fulfillment of cooperative agreement number CR812588 by Indiana University under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from April 27, 1987 to August 26, 1990, and work will be completed as of October 26, 1990.

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ABBREVIATIONS

D4	Tetrachlorodibenzo-*p*-dioxin
D5	Pentachlorodibenzo-*p*-dioxin
D6	Hexachlorodibenzo-*p*-dioxin
D7	Heptachlorodibenzo-*p*-dioxin
D8	Octachlorodibenzo-*p*-dioxin
ECNI	Electron capture negative ionization
ECD	Electron capture detector
F4	Tetrachlorodibenzofuran
F5	Pentachlorodibenzofuran
F6	Hexachlorodibenzofuran
F7	Heptachlorodibenzofuran
F8	Octachlorodibenzofuran
GC	Gas chromatography
GC/MS	Gas chromatographic mass spectrometry
GFF	Glass fiber filter
H	Henry's law constant
H_A	Heat of adsorption
K_{ow}	Octanol-water partition coefficient
L	Latent heat of vaporization
P	Particle-bound phase
p^*	Particle-bound fraction
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-*p*-dioxins
PCDD/F	PCDD and PCDF
PCDF	Polychlorinated dibenzofurans
P_o	Vapor pressure
P_o^l	Sub-cooled liquid vapor pressure
P_o^s	Solid-phase vapor pressure
P_{gc}	Vapor pressure by GC method
PUF	Polyurethane foam
R	Gas constant
RI	Retention index
S_p	Surface area of particles per volume air
T	Ambient temperature
T_m	Melting temperature
t_r	Retention time
TSP	Total suspended particles
V	Vapor phase
V/P	Vapor-to-particle-bound ratio
V_d	Deposition velocity
W	Total washout ratio
W_g	Gas washout ratio
W_p	Particle washout ratio

CHAPTER 1

BACKGROUND INFORMATION

INTRODUCTION

It might be argued that dioxin is the chemical most feared by the public. Although there are, in fact, 75 different congeners of the polychlorinated dibenzo-*p*-dioxins (PCDD) and 135 isomers of the related polychlorinated dibenzofurans (PCDF), in the public's mind dioxin means 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. This fame results from several facts: **(a)** this particular congener kills guinea pigs at a level of 0.6 μg/kg (Poland and Glover, 1977), making it the most toxic anthropogenic compound known; **(b)** this congener was a contaminant in the defoliant used in the Vietnam War, Agent Orange, at an average level of 2 ppm (Esposito *et al.*, 1980); and **(c)** this congener is linked to the contamination of Times Beach, Missouri (Carter, *et al*, 1975) and Seveso, Italy (Reggiani, 1979, 1980), a contamination which resulted in the permanent evacuation of these towns.

PCDD and PCDF have been found in fish (O'Keefe *et al.*, 1983; Ryan *et al.*, 1983; Stalling, *et al.*, 1985; Fehringer *et al.*, 1985); sediment (Czuczwa and Hites, 1986; Czuczwa *et al.*, 1984); and human adipose tissue (Ryan, 1986; Graham *et al.*, 1986; Needham *et al.*, 1987). This indicates that they are ubiquitous in the environment, and raises several questions. These questions include: **(a)** What is the geographic variability of the environmental concentrations? **(b)** What impact do PCDD/F have at these concentrations? **(c)** Where did they come from originally? **(d)** How did they get into the environment? **(e)** Will they degrade or migrate to some other location or environmental compartment? These questions can only be answered by detailed studies of PCDD/F in the various environmental compartments in which they are found.

A report of PCDD and PCDF in the sediment of a remote isolated lake (Czuczwa *et al.*, 1984) indicated that atmospheric transport was an important part of the picture. There are, however, only a few recent reports on PCDD and PCDF in the ambient atmosphere (Eitzer and Hites, 1986; Oehme *et al.*, 1986; Buck and Kirschmer, 1986; Nakano *et al.*, 1987; Rappe *et al.*, 1988; Smith *et al.*, 1988). None of these studies were of a sufficient detail to develop an understanding of the underlying physical characteristics of PCDD and PCDF which control their atmospheric transport and deposition. This study, therefore, was undertaken to fill this gap. Thus, this is the first detailed, long-term study of PCDD and PCDF in the ambient air and rain at a single location.

OBJECTIVES AND ORGANIZATION OF PROJECT

The goal of this project is to improve our understanding of the underlying parameters and characteristics that control the behavior of PCDD and PCDF as they are transported through the atmosphere from source to sink. To do this we measured the concentrations of PCDD and PCDF in ambient air and in rain samples; estimated the extent of geographic and temporal variability; and determined the parameters controlling transfer between environmental compartments.

The remainder of this chapter is devoted to background information. The first section covers the physical and toxicological characteristics of PCDD/F. Next, the current environmental concentration data for PCDD/F are discussed. This section introduces the concept of source-to-sink homologue profile transformations. Lastly, the analytical methods used to study the underlying parameters which control those transformations are discussed.

Chapter 2 focuses on the experimental aspects of this work. This chapter includes sections on sampling locations, sampling procedures, sample cleanup, mass spectrometry procedures, and quality assurance.

Chapter 3 reports on the vapor pressures of PCDD/F. It describes the experimental procedure used to determine the sub-cooled liquid vapor pressure of several PCDD/F. These values are then correlated to gas chromatographic (GC) retention indexes.

Chapter 4 discusses the experimental results for ambient air at the primary sampling location. The localized geographic and temporal variations are examined. The effects of temperature and vapor pressure on an individual congener's vapor-to-particle-bound concentration ratio are discussed.

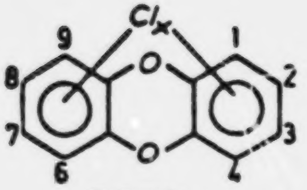
In chapter 5, the different environmental locations and compartments are compared to one another next. There are major sections in this chapter on the field estimation of washout ratios and Henry's law constants, geographic variability, and depositional flux determinations. Finally, the reported data from all compartments are compared in an interpretation of the observed changes in homologue profiles between the sources and sinks.

Finally, chapter 6 summarizes the observed phenomena and suggests areas for future research on topics related to this project.

PHYSICAL, CHEMICAL, AND TOXICOLOGICAL CHARACTERISTICS

Structures

The structures and systematic numbering of PCDD and PCDF are given in Figure 1-1. Each numbered position can be occupied by either a chlorine or a hydrogen atom. There are several terms describing the compounds which should be defined. Two compounds are congeners if they have the same backbone structure (i.e., dioxin or furan); they are isomers if they have the same number of chlorine atoms as well as the same backbone; homologues (or congener classes) represent all the isomers of one level of chlorination lumped together. Thus, there are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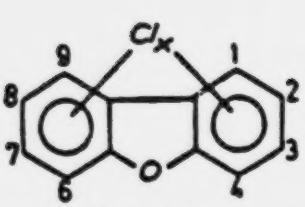
PCDD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PCDF

Figure 1-1. Structures and position numbers for the polychlorinated dibenzo-*p*-dioxins (top) and polychlorinated dibenzofurans (bottom).

75 congeners of PCDD, 22 isomers of tetrachlorodioxin, and 1 tetrachlorodioxin homologue.

Physical-Chemical Properties

To study transport and deposition processes for a compound, it is necessary to know or estimate several physical-chemical properties. For atmospheric processes, vapor pressure is a most important parameter. Similarly, for water-related processes, such as rainfall and transfer through the water column to sediment, such parameters as water solubility, the octanol-water partition coefficient (K_{ow}), and the Henry's law constant (H) are important. The values of these parameters are dependent on the position and number of chlorine atoms on the PCDD/F.

Recent reports on physical-chemical properties of PCDD and PCDF only give data for a few selected congeners (Sarna *et al.*, 1984; Friesen *et al.*, 1985; Schroy *et al.*, 1985; Rordorf, 1985, 1987, 1988; Burkhard and Kuehl, 1986; Marple *et al.*, 1986; Shiu *et al.*, 1988). Because 2,3,7,8-tetrachlorodioxin is the single most toxic congener, it is usually included in these reports. Unfortunately, other congeners are not consistently included. However, these reports allow us to estimate the ranges of the important parameters. These are presented in Table 1-1. For all of the parameters, there is a consistent direction of change with increasing level of chlorination. Thus, vapor pressures, solubilities, and Henry's law constants decrease with level of chlorination while K_{ow} increases.

The limited number of PCDD/F congeners with measured vapor pressures is a severe deficiency. We need these values if we are to study the atmospheric behavior of a compound. Thus, one part of this project determines the sub-cooled liquid vapor pressures for these compounds. A second part of this project estimates Henry's law constants of the homologues from the atmospheric measurements.

Toxicological Properties

There is an extensive body of literature on the toxicological effects of PCDD and PCDF. Several important points will be discussed here, but for further information, the reader should consult the extensive review in the *Health Assessment Document for Polychlorinated Dibenzo*-p-*dioxins* published by the EPA in September, 1985. The important points are as follows:

(a) The acute toxicities of PCDD/F are highly species-dependent. For example, while the dose that is lethal to 50% of test subjects (LD_{50}) for 2,3,7,8-tetrachlorodioxin in guinea pigs is 0.6 μg/kg, in hamsters it is 5000 μg/kg (Kociba and Schwetz, 1982).

(b) The acute toxicity is highly dependent on the number and position of the chlorine atoms. Thus, while 2,3,7,8-tetrachlorodioxin has an LD_{50} of 3 μg/kg, moving the chlorine from position 3 to position 4 raises the LD_{50} to 990 μg/kg (McConnell *et al.*, 1978). In general the most toxic isomers are those in which all of the 2, 3, 7, and 8 positions are occupied by chlorine atoms.

(c) Animal studies indicate the potential for chronic effects. Reported effects include teratogenic effects such as increased formation of cleft palate (Moore *et al.*, 1973) and carcinogenic effects, though the degree to which PCDD

Table 1-1. Measured Value Ranges for Selected PCDD and PCDF Properties.[a]

Property	Cl range	# congeners	range of values	reference
Aq. Sol.	4-8	6	3.2×10^{-7}-4×10^{-10} g/L	Friesen *et. al.*, 1985
Aq. Sol.	1-8	14	4.1×10^{-6}-4×10^{-10} g/L	Shiu *et. al.*, 1988
Aq. Sol.	1	1	3.1×10^{-7} g/L	Schroy *et al.*, 1985
log K_{OW}	1-8	13	5-13	Sarna *et al.*, 1984
log K_{OW}	4	5	5.8-7.2	Burkhard and Kuehl, 1986
log K_{OW}	1-8	15	4.8-8.2	Shiu *et. al.*, 1988
Vap. Press.	1-8	13	9×10^{-5}-8×10^{-13} torr	Rordorf, 1985,1987
Vap. Press.	4	1	3.5×10^{-9} torr	Schroy *et. al.*, 1985
Henry's Const.	1-8	14	14.8-0.68 Pa m^3/mole	Shiu *et. al.*, 1988

[a] Values are reported from 20-30°C. When a range is given, the first value represents the value for the lower chlorinated congener, and the second value is for the more chlorinated congener.

and PCDF act as tumor promoters or initiators is still debatable (U. S. EPA, 1985). Other subchronic effects include liver toxicity, thymic atrophy (possibly related to immune response), and weight loss (Kociba and Schwetz, 1982).

(d) Human studies are limited to contamination incidents or epidemiological studies, and thus, these studies either have a very limited number of highly exposed individuals or larger numbers of lightly exposed individuals. There are great difficulties in sorting out etiological factors. The most frequently observed effect in humans with acute exposure is chloracne (Taylor, 1979). The only evidence of a human carcinogenic effect is an increased incidence of soft-tissue carcinomas (Hardell and Sandstroem, 1979; Erickson *et al.*, 1981). Vietnam veteran studies have been inconclusive due to difficulties in determining a specific individual's exposure and in eliminating other effects (the so-called Vietnam experience). The study most likely to report effects from Vietnam is the Ranch Hand study of the personnel who actually handled Agent Orange. The latest report from this study shows an increased incidence of skin cancer, but it could not be attributed to dioxin because of the lack of full clinical dioxin syndrome attributes (for example, there were few positive indications of chloracne, a known effect) (Albanese, 1988).

ENVIRONMENTAL CONCENTRATIONS

Studying the fate of PCDD/F in the environment requires knowing their concentrations in various environmental compartments. These compartments can be broken into three categories: sources, transport media, and sinks.

Sources

There are two classes of PCDD/F sources to the environment. In the first, the PCDD/F are produced as unwanted byproducts of a chemical manufacturing process and are subsequently distributed with the product or its waste stream. The second class of sources is those in which combustion processes produce the PCDD/F which are subsequently distributed through the environment along with the combustion effluents.

The first class of sources has often been tied to specific environmental contamination episodes. To illustrate the possible environmental contamination from these sources, I will discuss two chemicals which caused several of these episodes. These are the chlorophenols and the polychlorinated biphenyls (PCB).

Chlorophenols are precursors to several products, one of which is 2,4,5-trichlorophenoxyacetic acid (one of the herbicides in Agent Orange). Thus dioxins, which are contaminants in chlorophenols, have been dispersed with the use of herbicides. Chlorophenol production also resulted in the contamination (and subsequent evacuation) of Seveso, Italy, following the explosion of a reactor producing 2,4,5-trichlorophenol (Reggiani, 1979, 1980) and the contamination (and subsequent evacuation) of Times Beach, Missouri, with waste oil from a 2,4,5-trichlorophenol plant (Carter *et al.*, 1975).

PCDF were trace impurities in various PCB formulations. Thus, wherever PCBs were used and disposed, there is the potential for a PCDF source. In one of the more noted contamination incidents, the "Yusho" incident, in which more than 1000 people consumed PCB-contaminated rice oil, there were significant PCDF residues in the tissues of those exposed (Nagayama *et al.*, 1977).

These industrial sources are important when considering specific contamination incidents. They can lead to significant human exposure which can require drastic action, such as the evacuation of a town. They do not, however, explain the ubiquity of PCDD/F in the environment. Industrial sources cannot explain the finding of PCDD/F in remote locations that have not had specific contamination incidents (Czuczwa *et al.*, 1984). Thus, to study the ubiquity of PCDD/F in the environment, we must examine in detail the second class of sources. These are the combustion sources, from which emissions would directly lead to atmospheric dispersion throughout the environment.

There are many possible combustion sources of PCDD/F. The so-called "Trace Chemistries of Fire" theory states that PCDD/F are formed and found on particles produced by almost all fires (Bumb *et al.*, 1980). However, Czuczwa and Hites (1986) showed that the great preponderance of PCDD/F in background environmental samples is from the combustion of chlorinated organic compounds. The formation process can occur whenever these compounds are burned, whether it be as discarded plastics in a municipal waste incinerator or some more direct process. This report will not examine whether or not there is a *de novo* synthesis of these compounds or if specific precursor compounds are necessary. It will, instead, focus on the mixture of PCDD/F produced by the various combustion sources.

The most commonly reported combustion sources are municipal waste incinerators (Buser and Bosshardt, 1978; Bumb *et al.*, 1980; Lustenhouwer *et al.*, 1980; Cavallaro *et al.*, 1982; Liberti and Brocco, 1982; Liberti *et al.*, 1982; Olie *et al.*, 1982; Rappe *et al.*, 1983, 1985, 1986; Tong and Karasek, 1986; Yashuhara *et al.* 1987; Clement *et al.*, 1988). Other combustion sources include industrial waste incinerators (Buser and Bosshardt, 1978; Scheidl *et al.*, 1986) and sewage sludge incinerators (Clement *et al.*, 1987). PCDD/F have been found in motor vehicle emissions (Marklund *et al.*, 1987), and they have been detected in used motor oil (Ballschmiter *et al.*, 1986).

It is useful to compare the relative amounts of the homologues produced by different combustion sources. This is shown in Figure 1-2 for an industrial waste incinerator (Buser and Bosshardt, 1978), two different municipal waste incinerators (Rappe *et al.*, 1983; Clement *et al.*, 1988) (one at two different operating conditions), and motor oil from a gasoline-powered car (Ballschmiter *et al.*, 1986). The bars represent the concentrations of the tetrachloro- through octachloro- furan and dioxin homologues. Note that each source gives a different homologue emission pattern; no homologue consistently dominates the pattern. In fact, even the same source (A-1 and A-2) produces different patterns when the operating conditions are changed. Also note that octachlorofuran is never in high relative abundance. Clearly, the relative abundances of the homologues are highly variable; they depend on such parameters as fuel, combustion temperature, and amount of excess oxygen. Thus, there is a highly variable input into the atmosphere.

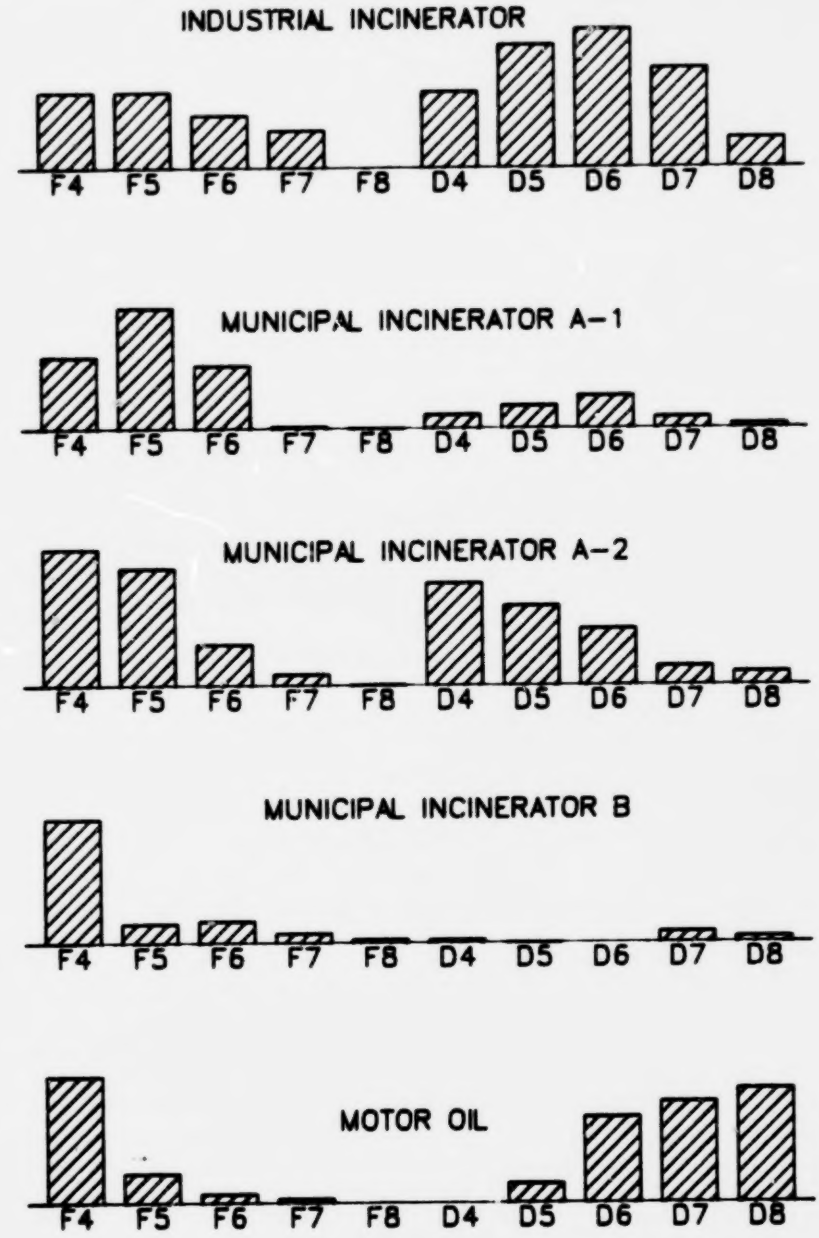


Figure 1-2. Homologue profiles from combustion sources of PCDD/F: industrial incinerator from Buser and Bosshardt (1978); municipal incinerator A, tests 7 and 14 from Clement *et al.* (1988); municipal incinerator B from Rappe *et al.* (1983); and motor oil of a gasoline powered car from Ballschmiter *et al.* (1986). The bars represent the relative concentrations of the tetra-, penta-, hexa-, hepta-, and octachlorofurans (F4, F5, F6, F7, and F8, respectively) and the tetra-, penta-, hexa-, hepta-, and octachlorodioxins (D4, D5, D6, D7, and D8, respectively).

Transport Media

The transport media on which this project focuses is the atmosphere. Other media, such as groundwater or rivers, which could be important for a specific contamination incident, will not be discussed here. There are several recent reports of PCDD/F in ambient air (Eitzer and Hites, 1986; Oehme *et al*., 1986; Buck and Kirschmer, 1986; Nakano *et al*., 1987; Rappe *et al*., 1988; Smith *et al*. 1988), but, these reports have been limited in the number of samples and time span sampled. In addition, most of these reports have not considered the multiple phases present in the atmosphere. Thus, this project is the first to extensively study this environmental compartment.

These other reports can, however, be used in assessing the nature of the problem. Figure 1-3 shows the homologue profiles found in ambient air at four urban locations (Buck and Kirschmer, 1986; Nakano *et al*., 1987; Rappe *et al*., 1988; Smith *et al*., 1988). Although there is still some variability in the homologue profiles, the samples show some similarities. The samples all tend to have higher relative concentrations of the F4, F5, D7, and D8 homologues and lower relative concentrations of the F8 and D4 homologues. The total concentrations in these samples range from about 10 to 30 pg/m^3. From these measurements, it is clear that the sensitivity of the chosen analytical scheme must be maximized.

Sinks

There are two sinks which should be considered. The first is a primary environmental sink, lake sediment. The second is the ultimate sink of concern to man, his own body. Both of these compartments have been studied.

Homologue profiles for sediment from 4 lakes (Czuczwa, 1984) and for the average of 46 human fat samples (Ryan, 1986) are presented in Figure 1-4. These homologue profiles show great similarities to one another. All have octachlorodioxin as the most abundant homologue, lower concentrations of the F7 and D7 homologues, and little of the other congeners. The consistency of this pattern suggests a common input to these sinks.

Summary

Comparing the three sets of homologue profiles representing the sources, transport medium, and sinks defines the question which this report hopes to answer. Homologue profiles are transformed from a highly variable state in the sources to a very consistent pattern in the sinks. Thus, there are obviously forces acting during the atmospheric transport and deposition process which are causing transformations to occur. It is, therefore, the goal of this project to study the atmospheric transport process in detail and to improve our understanding of those transformations and the underlying characteristics of PCDD/F which control them. This will be done by determining the concentrations of PCDD/F in the transport and deposition media (i.e., air and rain) over time and space. The samples will be compared and contrasted over time, location, and environmental compartment. These comparisons should illuminate trends so that the characteristics of PCDD/F controlling the transformations can be determined.

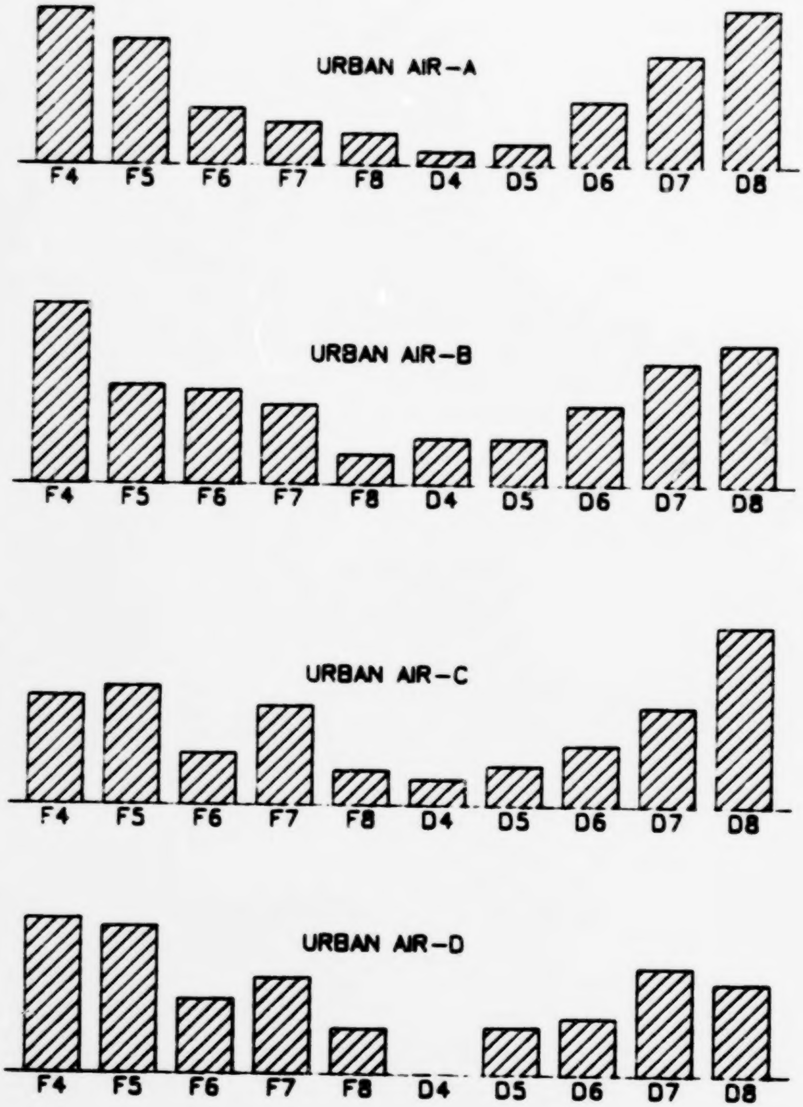


Figure 1-3. Homologue profiles of PCDD/F from ambient urban air at four different locations (see Figure 1-2 for abbreviations). Data from: A. Buck and Kirschmer (1986), total concentration 8.7 pg/m^3. B. Nakano *et al.* (1987), total concentration 17 pg/m^3. C. Rappe *et al.* (1988), total concentration 29 pg/m^3. D. Smith *et al.* (1988), total concentration 20 pg/m^3.

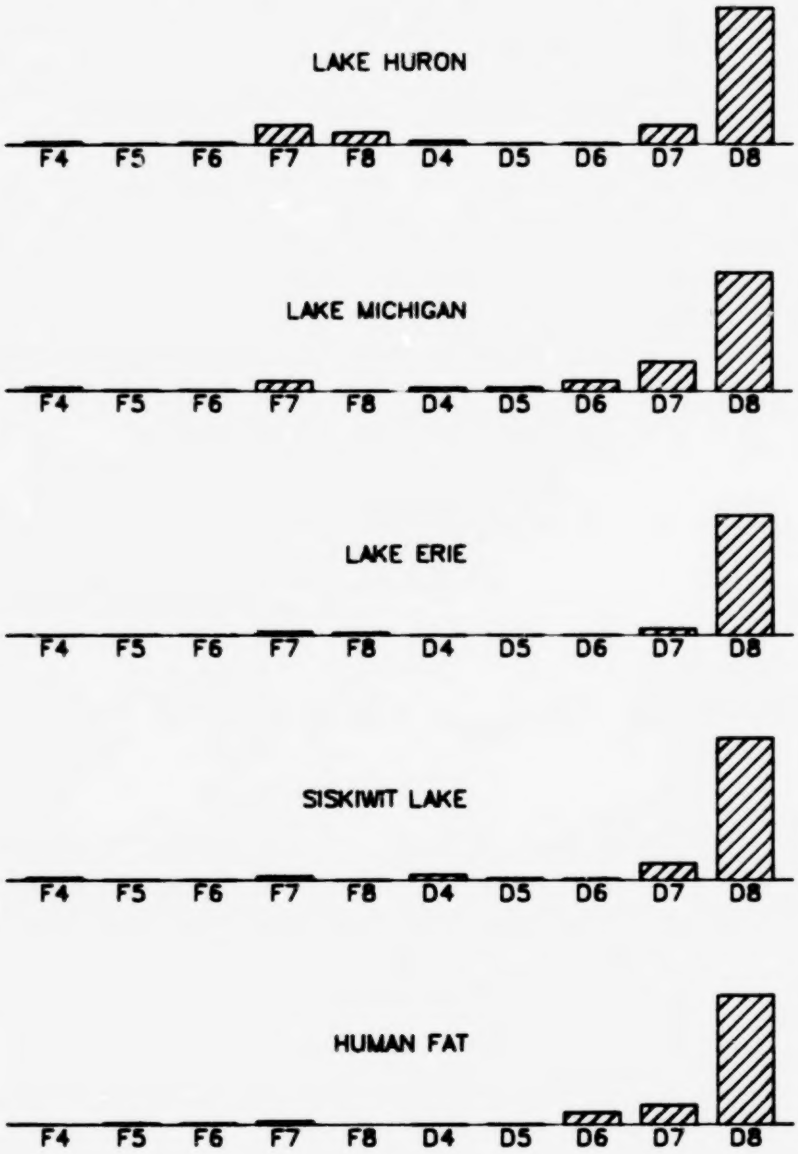


Figure 1-4. Environmental sink homologue profiles of PCDD/F. All sediment samples are the top most sediment layer reported from a sediment core in Czuczwa (1984). Human adipose tissue is an average of 46 samples as reported by Ryan (1986). Total concentrations are: Lake Huron, 470 pg/g; Lake Michigan, 780 pg/g; Lake Erie, 2000 pg/g; Siskiwit Lake, 720 pg/g; human fat, 1100 pg/g.

AMBIENT AIR AND RAIN ANALYSES

There is a large volume of literature on the analysis of ambient air and rain. The literature ranges from theoretical discussions of deposition velocity based on particle size to field measurements. An exhaustive review of this literature is beyond the scope of this report; the discussion that follows, therefore, will focus on methods used in this study.

Air

Organic species are present in air as two coexisting phases. Compounds can be present as a vapor phase, or they can be bound to particles. Junge (1977) developed a theoretical model (based on adsorption theory) to explain the partitioning between the two phases for a semivolatile organic compound. His model states:

$$p^* = cS_p/(P_o + cS_p) \qquad (1\text{-}1)$$

where p^* is the particle-bound fraction; c is a constant dependent on molecular weight and heat of condensation; S_p is the surface area of particles per volume air; and P_o is the saturation vapor pressure of the compound. From this model, he calculated a series of curves for different vapor pressures on a p^* vs. S_p plot. This graph is reprinted here as Figure 1-5. From this graph and the character of the site (i.e., urban or rural), p^* can be estimated for different vapor pressures.

Vapor pressure is usually reported for pure solids. In the ambient atmosphere it is unlikely that anthropogenic organic compounds reside on the particles as a crystalline phase (Mackay *et al.*, 1986; Bidleman, 1988). In fact, adsorption of semivolatile organics to particles has been shown to correlate better with the subcooled liquid vapor pressures (P_o^l) (the liquid vapor pressure extrapolated below the melting point) than with the pure solid-phase vapor pressure (P_o^s) (Bidleman and Foreman, 1987; Bidleman, 1988). This indicates that these compounds are spread about the particles in a quasi-liquid state. The two vapor pressures can be converted as shown by Mackay *et al.* (1982):

$$\ln(P_o^l/P_o^s) = 6.8\,(T_m\text{-}T)/T \qquad (1\text{-}2)$$

where T_m is the melting temperature of a compound; T is the ambient temperature; and 6.8 is an empirical constant related to the entropy of fusion.

Converting the solid-phase vapor pressures reported in Table 1-1 to the subcooled liquid vapor pressures requires knowledge of melting temperatures for PCDD/F. These show great variation (there is only a weak increasing trend with level of chlorination): they fall in the range from 150^o to 330^oC for congeners with more than four chlorine atoms (Rordorf, 1988). This means that at ambient temperatures, the solid vapor pressures from Table 1-1 are two to three orders of magnitude lower than those which should be used for environmental work. Thus, sub-cooled liquid vapor pressures in the range of 10^{-6} to 10^{-10} torr should be expected for congeners with greater than four chlorine atoms in the atmosphere. Using these values, Figure 1-5 shows that p^*'s for PCDD/F would range between 0.05 for the more volatile congeners in cleaner air to 0.99 for the less volatile

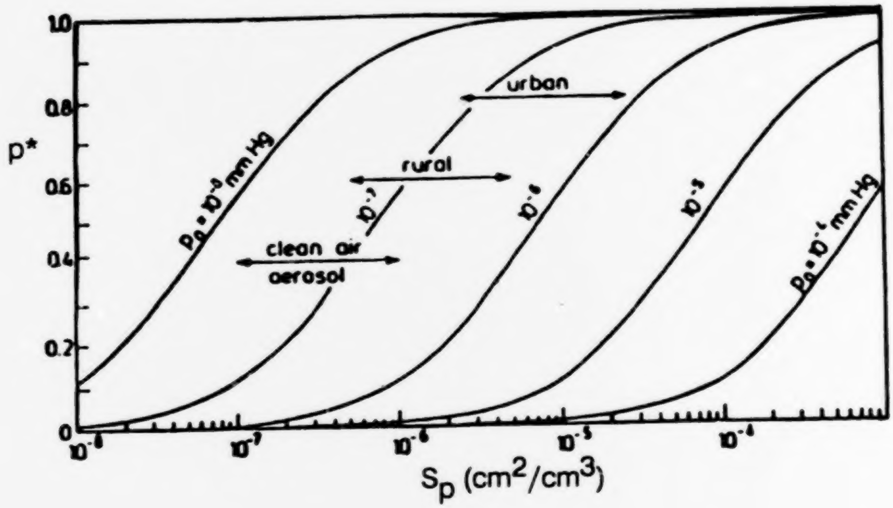


Figure 1-5. Estimated values of the particle-bound fraction as a function of the saturation vapor pressure and surface area of the particles. The calculations (see equation 1-1) are based on adsorption theory and are only order of magnitude estimates. (Reprinted from Junge, 1977.)

congeners in urban air. Therefore, both phases are likely to be present in ambient air samples.

Various processes, such as photodegradation and deposition, occur at different rates for the two phases. Thus, it is imperative that both phases be studied in order to understand the transformations that occur during atmospheric transport. Therefore, the sampling method must be able to separately collect the two phases. In addition, it is likely that at least one of the phases will be present at low concentrations (as indicated by both high and low p°'s). Thus, a large sample volume is desired so that the sensitivity can be maximized.

One ambient air sampling technique which meets these requirements is the use of two-stage high-volume air samplers. The first stage consists of a 0.1 μm glass fiber filter (GFF) to collect the particles, and the second stage consists of an adsorbent material to collect the vapor phase. There are several adsorbents which have been used for semivolatile organics: XAD-2, Tenax-GC, and polyurethane foam (PUF). Of these, the PUF is easiest to handle and has a low flow resistance; but it does have breakthrough problems with very volatile organics (Billings and Bidleman, 1980). PUF has been shown to be effective for pesticides, polycyclic aromatic hydrocarbons (PAH), and PCB (Lewis *et al.*, 1977; Turner and Glotfelty, 1977; Erickson *et al.*, 1978; Simon and Bidleman, 1979; Billings and Bidleman, 1980; MacLeod, 1981; Thrane and Mikalsen, 1981; Keller and Bidleman, 1984; Ligocki and Pankow, 1985; Bidleman *et al.*, 1987). Because PCDD/F are similar to these compounds, PUF appears to be quite suitable. Thus, the work reported here uses a high-volume air sampler equipped with a GFF and a PUF plug (for details, see Chapter 2).

Rain

The sampling of rain for organic components was recently reviewed in depth by Mazurek and Simoneit (1986). They report that the majority of precipitation samples were "bulk deposition" samples; that is, samples were taken with continuously open samplers which do not discriminate between wet and dry deposition. Furthermore, many of the wet-only samples do not divide the sample into the two constituent phases present in rain. These two phases are the dissolved and particle-bound phases.

Separation of the two phases can be achieved by filtering the rainwater. This filtration should ideally be performed as the rain is collected so that there is no time for organic compounds to transfer between the phases after sampling. Precipitation samplers with on-line filtration have been used to measure concentrations in both the dissolved and particle-bound phases for PAH, PCB, and other chloro-organic compounds (Murphy and Rzeszutko, 1977; Pankow *et al.*, 1984; Ligocki *et al.*, 1985a, 1985b; Villeneuve and Cattini, 1986; Leuenberger *et al.*, 1988). Given the similarity of these compounds to PCDD/F, it is likely that both phases would be present in the rain samples.

As rain forms in the atmosphere and falls to the earth, compounds are transferred from the air to the rainwater. This process is called rain scavenging. Its measure is washout, which is the ratio of the rain concentration to the air concentration on a volume-to-volume basis. Total rain washout is a function of both particle scavenging (cleaning the air of particles) and vapor scavenging (cleaning the air of vapors).

There have been several reviews of the scavenging process which occurs as rain falls through the atmosphere. Particle scavenging has a theoretical concentration factor of 10^6 based on physical parameters, such as the amount of water vapor which must agglomerate to a particle forming a raindrop (Slinn *et al.*, 1978), though empirical studies often report lower values (McMahon and Denison, 1979; Ligocki *et al.*, 1985b). Vapor scavenging is a function of the Henry's law constant of a compound (the ratio of vapor pressure to solubility) if equilibrium is reached between the vapor phase and the rain droplet (Slinn *et al.*, 1978; Ligocki *et al.*, 1985a; Bidleman, 1988). From the empirical measurements by Ligocki *et al.* (1985a) for several large PAH, a vapor scavenging efficiency somewhere between 10^4 to 10^5 might be expected for PCDD/F.

Even with these large concentration factors from air to rain, it is obvious from the low air concentrations that large rain samples must be collected. Thus, the sampling system used for this study was capable of collecting up to 18 L of rainwater. The system is described in Chapter 2.

SUMMARY

This chapter has presented background material on PCDD/F and reviewed the relevant literature. It showed that the transformations of PCDD/F occurring in the atmosphere are not well understood. Thus, the goal of the project is to determine the underlying characteristics of PCDD/F controlling those transformations. The remainder of this report will cover the experimental methods (Chapter 2), determination of vapor pressures of PCDD/F (Chapter 3), experimental results (Chapters 4 and 5), and a summary with recommendations for future work (Chapter 6).

CHAPTER 2

EXPERIMENTAL ANALYSIS METHODS

INTRODUCTION

This chapter will focus on the experimental methods used for the analysis of ambient air and rain samples. Thus, there are major sections on sampling, sample analysis, and quality assurance. The experimental work on vapor pressure determination is discussed in Chapter 3.

SAMPLING

There are several things to be considered when conducting research with environmental samples: What type of samples should be collected? Where is the best place to collect them? How are they best collected? The answer to these types of questions can be collectively grouped into the category of sampling. We have already discussed the types of samples we wanted to collect in Chapter 1 (ambient air and rain); thus, we will consider here only where and how they are collected.

Sampling Sites

The primary study location was Bloomington, Indiana. Bloomington is a city of approximately 50,000 people and the home of Indiana University. This location was chosen because there is a possibility that a municipal incinerator will be built which will also be used to combust PCB-contaminated materials. Thus, this study also provides baseline data against which the performance of this incinerator can be evaluated.

Air samplers were located on the roofs of four buildings in the Bloomington, Indiana, area (see Figure 2-1). Two of these sites corresponded to areas of high human population (the Courthouse and SPEA sites), and the other two corresponded to sites of high potential incinerator impact (the Sanders and Batchelor sites). The SPEA site was used for initial tests of the system and was discontinued in June, 1986. Sampling at the other sites started in September, 1986, (Courthouse) and December, 1986 (Sanders and Batchelor). The high incinerator impact areas were identified by the incinerator risk assessment (Westinghouse Electric Corporation, 1986). Rooftops were chosen as sampling sites to provide convenient access while minimizing security problems.

The rain sampler was located at the SPEA site. This sampler was altered over the course of the study to allow on-line filtration of the rain samples. Therefore, only data obtained subsequent to the alterations (the final year of the study) are included in this report.

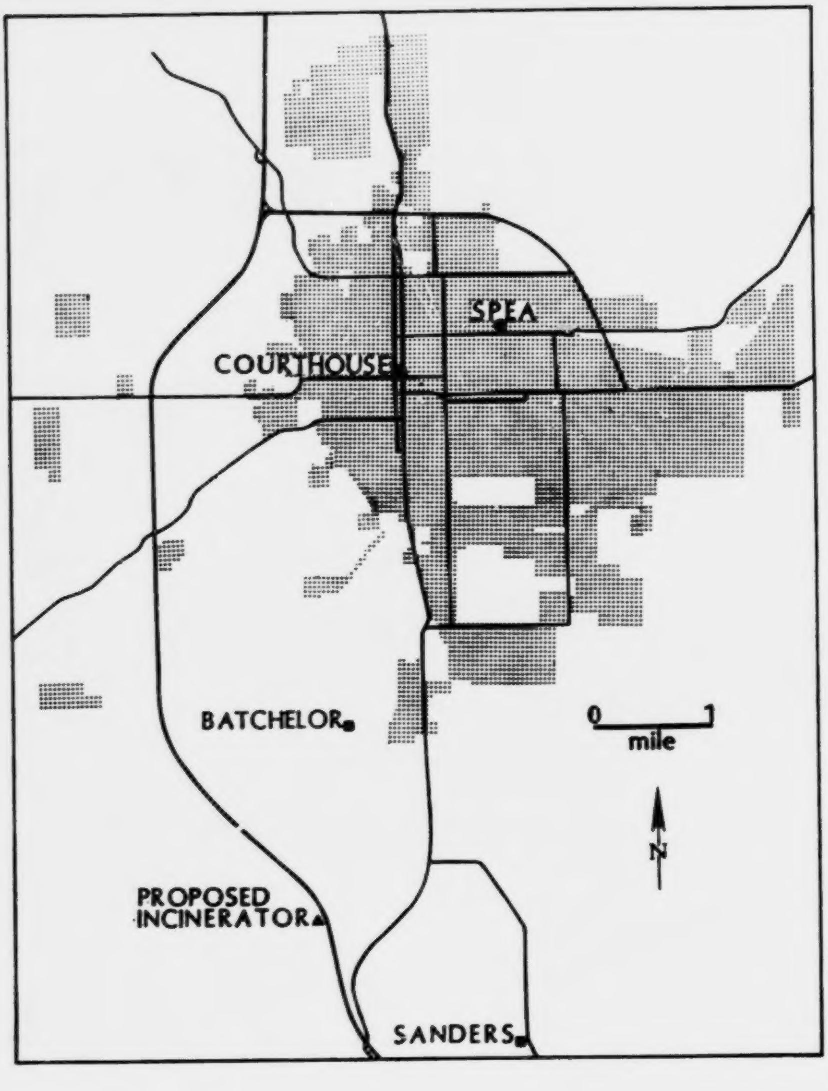

SPEA
COURTHOUSE
BATCHELOR
PROPOSED INCINERATOR
SANDERS
0
1
mile
N

Figure 2-1. Map of Bloomington, Indiana, showing the location of the four sampling sites and of the proposed incinerator.

Two sites outside of Bloomington were chosen for air samples from areas with higher and lower degrees of urbanization. These were Indianapolis, Indiana, a city with an approximate population of 800,000, and Trout Lake, Wisconsin, a forested area 100 km south of Lake Superior. These sites were sampled for 2-week periods: Indianapolis in November, 1987, and Trout Lake in August, 1987. Although only a few samples were obtained from these sites (four for Indianapolis and three for Trout Lake), they allowed an assessment of the geographic variability of the data.

Sample Collection

Air samples were collected at least on a monthly basis at each site with high-volume air samplers (Sierra-Misco, Berkeley, California, model 650) modified to collect both vapor and particle-bound phases. Air was first drawn through a glass fiber filter (GFF) and then through a polyurethane foam plug (PUF). Particles were collected on the GFF while vapors were absorbed by the PUF. The GFF was precleaned by baking it for 4 hr at 450°C. Both before and after sample collection, GFF's were dried in a desicator for 24 hr and weighed. Weight differences were used to determine the total suspended particle (TSP) concentration. GFF's were then Soxhlet-extracted with benzene for 24 hr. The PUF plugs were precleaned by Soxhlet extraction with acetone, methylene chloride, and petroleum ether for 24 hr each. After use, the PUF plugs were sealed in cans and stored at -40°C until they were Soxhlet-extracted for 24 hr with petroleum ether.

Sampler flow rates were calibrated with a venturi calibrator (Sierra-Misco, model 1080) every 3 months or whenever the samplers were moved or repaired. The flow rate was set prior to sampling at approximately 0.5 m^3/min and checked at the conclusion of sampling. Samples were taken over 2- to 3-day periods, giving volumes ranging from 1500 to 2400 m^3. Temperatures were monitored with a portable recorder. One data point every 3 hours was used to determine the average air temperature during the sampling period.

Rain samples were collected with a stainless steel 1-m^2 wet-only collector. A rain sensor opened the sampler and started a pump. The pump drove the rain through a series of three precleaned, 0.1 μm, GFF's into a 20-L glass carboy. Filters were used in series because the action of the pump often destroyed the first filter. The filters were Soxhlet-extracted in a 1:1 mixture of acetone and methylene chloride for 24 hr. The rainwater was liquid-liquid extracted with methylene chloride by stirring vigorously with a stir bar for 24 hr. The methylene chloride layer was removed and passed through 60 g of anhydrous sodium sulfate to remove most residual water.

SAMPLE ANALYSIS

Extracts of environmental samples often contain complex mixtures of organic compounds. When the desired analyte is a minor component, it is necessary to optimize the sensitivity and selectivity of the analytical method. These parameters are often played against one another; for example, increasing selectivity can decrease sensitivity. In gas chromatographic mass spectrometry (GC/MS), sensitivity can be increased by using selected ion monitoring; but, the cost is the loss of the complete mass spectrum, thus reducing selectivity.

The very low concentrations of PCDD/F in ambient air and rain samples require sensitivity to be the key parameter. Thus, it was decided to use electron capture, negative ion (ECNI) mass spectrometry rather than electron impact mass spectrometry which is often used for PCDD/F analysis. ECNI is an effective technique for the analysis of PCDD/F with more than four chlorine atoms because the PCDD/F's high degree of chlorination leads to high electron affinities, which in turn, enhances negative ion formation.

Sample Cleanup

Prior to extraction, all samples were spiked with two fully carbon-13 labeled isotopic compounds: 1,2,3,7,8-pentachlorodibenzofuran and octachlorodibenzo-*p*-dioxin (Cambridge Isotope Laboratories, Woburn, Massachusetts; KOR Isotopes, Cambridge, Massachusetts). These compounds were used as internal standards. It was assumed that any losses that occurred during sample extraction and cleanup were identical for the standards and the analytes.

Sample extracts were solvent-exchanged to hexane and concentrated to 5 mL in a rotary evaporator. The extracts were then taken through a two-step column chromatographic cleanup procedure developed by Czuczwa (1984). This was necessary because interfering compounds, such as PCBs, would be present at much higher concentrations than the PCDD/F and would compete for electrons in the negative ion mode of the mass spectrometer, thus reducing accuracy and sensitivity.

The extracts (in hexane) were passed through a 1.5 x 20-cm column packed with silica gel, activated at 160°C for 16 hr and then deactivated with 1% by weight of water and equilibrated for 16 hr. The samples were eluted with 75 mL each of hexane, 15% methylene chloride in hexane, and methylene chloride. The PCDD/F were collected in the second fraction, which was solvent-exchanged to hexane and reduced to less than 1 mL. This sample was then passed over a 0.5 x 6.5-cm micropipet packed with alumina, activated at 250°C for 2 hr and then deactivated with 1% by weight of water and equilibrated for 16 hr. The sample was eluted with 8 mL each of hexane, 2% methylene chloride in hexane, and 40% methylene chloride in hexane. The PCDD/F were present in the third fraction, which was collected in an 8-mL sample vial. The purified extracts were concentrated to a final volume of approximately 50 μL by slowly passing purified N_2 over the sample prior to analysis by GC/MS.

Quantitation by Homologue

All samples were analyzed on a Hewlett-Packard 5985B GC/MS system. A temperature-programmed (splitless injection at 60°C, isothermal for 2 min, 30°C/min to 210°, 2°C/min to 280°, isothermal for 10 min), 30-m x 0.25-mm, DB-5, fused silica column (J&W Scientific, Folsom, California), with helium as the carrier gas, was used to separate the PCDD and PCDF. The mass spectrometer was operated in the ECNI mode with methane as the reagent gas. The ion source pressure was 0.43 torr, and the ion source temperature was 150°C. Selected ion monitoring was used to further enhance sensitivity. Two ions from the most intense cluster of the mass spectrum of the tetrachloro- through octachloro- homologues were monitored. A peak was classified as a dioxin or furan only if the intensities of the two ions were in the proper ratio as predicted by the isotopic abundances.

A standard solution was made from the two carbon-13 standards (see above) and 23 different congener standards, 1234-D, 2378-D, 12347-D, 12378-D, 123478-D, 123678-D, 123789-D, 1234678-D, 12346789-D, 1278-F, 2378-F, 2348-F, 12378-F, 23478-F, 12389-F, 123478-F, 123678-F, 123789-F, 234678-F, 123489-F, 1234678-F, 1234789-F, 12346789-F (obtained either individually or in mixtures from Cambridge Isotope Labs). This solution was used to develop response factors relative to the two carbon-13 internal standards. The responses of the tetra-, penta-, and hexa-compounds were determined relative to carbon-13 12378-F, and those of the hepta- and octa- compounds were determined relative to carbon-13 octachlorodioxin. The response factors for compounds with the same number of chlorine atoms (isomers) were averaged together. Thus, 10 response factors for the tetra- through octa-dioxin and furan homologues were generated. Because ECNI is prone to shifting response factors with mass spectrometric conditions, the response factor standard solution was run every day that samples were run. Concentrations were determined by using the response factors, the ratio of the areas for the labeled and unlabeled peaks, and the known amount of internal standards.

Quantitation by GC/MS Peak

The data consistently showed the same dioxin and furan GC/MS peaks in the analyzed air samples. These were quantitated by apportioning the homologue concentrations among the GC/MS peaks of that homologue by their peak height (except for the tetrachlorodioxins, which did not have the consistency in peak pattern necessary for this approach). The rain samples, being closer to detection limits, were only analyzed by homologue.

Retention indexes for each standard (see above) were determined. These data were used to determine the retention indexes of each peak quantified. These data were then compared to published retention indices for the dioxins (Donnelly *et al.*, 1987) and the furans (Hale *et al.*, 1985). Unfortunately, differences in temperature programs and column lengths caused slight differences between the published retention indexes and those reported here. Using known standards compensated for some of these differences, allowing many congener identifications to be assigned to specific GC/MS peaks. However, other congeners could not be specifically assigned. Because of nonassigned congeners and multicongener GC/MS peaks, the data were analyzed by peak rather than by congener.

It was assumed that all congeners with the same number of chlorine atoms give the same response factor under ECNI conditions. This is not always true; for example, 2378-D gives a particularly low ECNI response. However, this limitation was accepted because ECNI considerably enhanced the sensitivity for most congeners.

The substantial concentration factor of the analytical method (greater than 2000 m^3 of air is represented in a final volume less than 50 μL) combined with the sensitivity of ECNI gives a limit of detection of less than 1 fg/m^3 with a 2-μL injection at optimum mass spectrometric conditions for air samples. Changes in mass spectrometric conditions, such as ion source cleanliness, can cause less than optimum performance, but sensitivity was never worse than 3 fg/m^3. This is a substantial improvement over the 10 to 20 fg/m^3 reported by Rappe *et al.* (1988) and Smith *et al.* (1988). Similarly rain samples had a limit of detection of 0.1 pg/L.

Data Reduction

Quantitation of 64 peaks in two atmospheric phases or 10 homologues in two rain phases for each sample resulted in a very large database, which required systematic reduction so that conclusions could be drawn. This data reduction was done using the Statistical Analysis System (SAS Institute Inc., Cary, North Carolina). The univariate procedure showed that the data's distribution approached lognormal rather than normal; thus, geometric means were used in averaging of data. A 0.05-fg/m^3 value was used for "not detected" levels in the geometric average for air samples. Correlation procedures showed that, within a homologue, any peak correlated with any other peak with >95% confidence. Thus, data analysis at the homologue level was used to significantly reduce the volume of data for much of the analysis.

QUALITY ASSURANCE

Accuracy for the complete procedure could not be checked because there is no PCDD/F air or rain standard. Different parts of the procedure could, however, be checked with various quality assurance procedures. These include duplicate samples, blank samples, breakthrough samples, and checks of the GC/MS method.

Duplicate Samples

Air samples taken by two samplers operating side by side were used to determine precision. From these paired sample sets it was determined that the precision of the entire method averaged 30%. Samples with concentrations near the detection limits showed worse precision than samples with concentrations significantly higher than the detection limits.

Blank Samples

One field blank was analyzed for at least every six samples. This sample was taken through the complete procedure from setup to mass spectrometry. Octachlorodioxin was the only component consistently in the air sample blank. This was corrected for by subtracting 30 fg/m^3 from every reported octachlorodioxin value.

Breakthrough Samples

A PUF plug acts as a frontal chromatography column. Thus, there is a finite limit on sample size beyond which compounds would elute off the plug at the same rate that fresh material is absorbed. This volume was not rigorously determined, but several PUF plugs were cut in half, with the front and back half analyzed separately. These samples all showed the PCDD/F to be retained only in the front half, indicating that the sampled volumes were well below the breakthrough volume.

GC/MS Method

A gauge of the accuracy of the mass spectrometric method is given in Table 2-1, which compares ECNI results obtained in our laboratory with results determined by high-resolution mass spectrometry on an EPA quality assurance sample (Harless, 1988). Except for the tetra-dioxin homologue, which we rarely see in our samples, the results are in reasonable agreement. The average percent difference is 17%. The duplicate samples analyzed here had an average 5% difference in the homologue values. This indicates that the mass spectrometry did not cause a major portion of the differences in duplicate samples.

SUMMARY

This chapter has focused on the experimental procedures used for the analysis of ambient air and rain samples. The use of high-volume air samplers and a large, wet-only rain sampler led to large concentration factors and gave us very low detection limits (1 fg/m^3 in air and 0.1 pg/L in rain). The chosen analytical techniques were shown to have good accuracy and precision.

Table 2-1. Homologue concentrations determined by ECNI *versus* concentrations determined by HRMS[a]

Homologue	ECNI[b]	HRMS[c]	% Difference
F4	33.2	43.1	26
F5	60.7	67.2	10
F6	60.8	53.0	14
F7	36.8	51.1	33
F8	6.8	7.5	10
D4	2.2	14.6	150
D5	25.0	32.8	27
D6	58.9	51.2	14
D7	52.7	61.9	16
D8	41.0	38.7	6
			avg = 17%[d]

[a] Comparisons performed by the EPA at Research Triangle Park (Harless, 1988). The data show the nanograms of a given homologue in a control sample made by the EPA.

[b] Average of two measurements.

[c] Average of three measurements.

[d] Excluding D4.

CHAPTER 3

MEASUREMENT OF VAPOR PRESSURES OF PCDD/F

INTRODUCTION

Semivolatile organic compounds are present in the atmosphere in a mixture of two phases (see Chapter 1): the vapor phase and the particle-bound phase. The extent to which a given compound is found in one phase in preference to the other phase is related to that compound's vapor pressure (Junge, 1977). Thus, if we are to study PCDD/F in the ambient atmosphere, it is essential that we know their vapor pressures at ambient temperatures. These are not known for all congeners; therefore, we have determined them as part of this project.

The vapor pressure of compounds of low volatility are normally determined by either gas saturation (OECD, 1981; Spencer and Cliath, 1983; Sonnefeld *et al.*, 1983) or effusion (Murray *et al.*, 1974; OECD, 1981; Spencer and Cliath, 1983) methods. These methods require pure compounds in measurable quantities, and thus, they are not applicable to costly and toxic compounds such as PCDD/F. Gas chromatography is an alternative method for measuring vapor pressures (Hamilton, 1980; Westcott and Bidleman, 1981; Bidleman, 1984; Kim *et al.*, 1984; Foreman and Bidleman, 1985). This method can be used for mixtures of compounds at low concentrations, thus reducing the problems stated above. It is based on the use of a nonpolar stationary phase and isothermal conditions such that the compound's GC retention time is directly related to its vapor pressure. The method has been used to study PCBs (Westcott and Bidleman, 1981; Bidleman, 1984; Foreman and Bidleman, 1985), herbicide esters (Hamilton, 1980), and organophosphorus pesticides (Kim *et al.*, 1984).

THEORY

The relevant equations for determining vapor pressure by the GC (hereafter called P_{gc}) method have been developed by Hamilton (1980). At a constant temperature, the vapor pressures (P_o) of a test and reference compound (1 and 2, respectively) are related by the ratio of their latent heats of vaporization:

$$\ln(P_{o,1}) = (L_1/L_2)\ln(P_{o,2}) + C \qquad (3\text{-}1)$$

where L is the latent heat of vaporization and C is a constant. These vapor pressures are also related to their GC retention times:

$$\ln(P_{o,1}) = \ln(P_{o,2}) - \ln(t_{r,1}/t_{r,2}) \qquad (3\text{-}2)$$

where t_r is the retention time. Combining and rearranging equations 3-1 and 3-2 yields:

$$\ln(t_{r,1}/t_{r,2}) = (1 - L_1/L_2)\ln(P_{o,2}) - C \qquad (3\text{-}3)$$

Therefore, a plot of $\ln(t_{r,1}/t_{r,2})$ *versus* $\ln P_{o,2}$ would have a slope of $(1 - L_1/L_2)$ and an intercept of (-C). Equation 3-1 can then be used to determine the vapor pressure of the test compound at any temperature, given the vapor pressure of the reference compound at that temperature.

Bidleman (1984) has shown that vapor pressures determined by the GC method correlate with sub-cooled liquid vapor pressures rather than with solid-phase vapor pressures. Thus, P_{gc} values can be considered estimates of P_o^l. This should prove particularly useful because (as discussed in Chapter 1) adsorption of semivolatile organics to particles in the atmosphere is a function of the sub-cooled liquid vapor pressure (Mackay *et al.*, 1986; Bidleman and Foreman, 1987; Bidleman, 1988).

EXPERIMENTAL

The use of a short capillary column and an electron capture detector (ECD) allows the detection of nanogram concentrations of dioxins and furans at temperatures ranging from 90°C to 150°C. The vapor pressure at 25°C can then be estimated through extrapolation of the data.

Standards used for this study were 1234-D; 12346789-D (Foxboro/Analabs, North Haven, Connecticut); 12378-D; 123478-D (KOR Isotopes, Cambridge, Massachusetts); 1234678-D; 2378-F; 12378-F; 23478-F; 123478-F; 123678-F; 123789-F; 234678-F; 1234678-F; 1234789-F (Cambridge Isotope Laboratories, Woburn, Massachusetts); and p,p'-DDT (EPA, Research Triangle Park, North Carolina). Samples were analyzed on a Carlo-Erba Fractovap series 4160 GC with a 0.75-m J&W, DB-5, 0.25 μm film thickness capillary column with an ECD. The GC was operated isothermally at 10 degree intervals from 90° to 150° C; splitless injection was used; and the helium flow was set by maintaining the column head pressure at 0.35 kg/cm^2. Retention times were determined on an HP 3390 A integrator. All sample runs were made in duplicate; average retention times were used for calculations. Sample runs consisted of the entire set of dioxins or furans plus the p,p'-DDT standard. The runs on the furans had a pair of unresolved peaks (123478-F and 123678-F; 123789-F and 234678-F); for the calculations, it was assumed that the vapor pressures were the same for both.

RESULTS

The choice of p,p'-DDT as the reference standard was dictated by the need for a compound which would chromatograph in a manner similar to the PCDD/F, be readily detected by the ECD, and have vapor pressures known at the experimental temperatures. Average vapor pressures of p,p'-DDT at 25°C and at the experimental temperatures were determined by regression of the data presented in Balson (1947), Dickinson (1956), Spencer and Cliath (1972) and Rothman (1980); the resulting data are presented in Table 3-1. These workers used either an effusion (Balson, 1947) or gas saturation (Dickinson, 1956; Spencer and Cliath, 1972; Rothman, 1980) method to measure the solid-phase vapor pressure of p,p'-DDT from 20° to 100°C. These values were converted to sub-cooled liquid vapor pressure values by the use of Mackay *et al.*'s (1982) equation (see equation 1-2).

Table 3-1. Sub-cooled liquid (below 110°) and liquid vapor pressures of p,p'-DDT as a function of temperature

Temp°C	$-\log(P_o^l)$ (torr)
25	5.59
90	2.65
100	2.29
110	1.94
120	1.61
130	1.30
140	1.01
150	0.73

Table 3-2 shows the retention time data used in this study. From these data, the parameters in equation 3-3 were calculated by regression, and Table 3-3 shows these parameters and the experimentally determined P_{gc} values at 25°C.

This experiment only determined the vapor pressures of a selected few of the 210 different congeners of PCDD/F. However, since the method is based on GC retention times, published retention indexes of dioxins (Donnelly *et al.*, 1987) and furans (Hale *et al.*, 1985) on the same type of column can be used to determine the vapor pressure of all other congeners. Figure 3-1 is a plot of the retention index *versus* $\log(P_{gc})$ at 25° C for each of the congeners studied here. Regression of these data ($r = 0.99$) yields the following equation for calculating the vapor pressure from the published GC retention indexes (RI):

$$\log(P_{gc}) = (408 - RI)/319 \qquad (3\text{-}4)$$

As mentioned in Chapter 2, the published retention index data did not fully coincide with our measured retention indexes. Thus, alternatively, the P_{gc} data can be regressed against the retention index data we determined for these standards using the GC temperature program used for our database. Regression of these data also showed $r = 0.99$, with the following equation:

$$\log(P_{gc}) = (517 - RI)/302 \qquad (3\text{-}5)$$

The two equations produce similar results. For example, Donnelly *et al.* (1987) report a retention index of 2781 for 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin while this work measured it as 2750. Using equations 3-4 and 3-5, respectively, yields vapor pressures of 3.6×10^{-8} torr and 4.0×10^{-8} torr, respectively. Because we could not identify precisely the retention index for all congeners, we felt that equation 3-4 was best used for comparisons with vapor pressures of PCDD/F reported in the literature, while equation 3-5 was best used for correlations with our database.

It is useful to compare the results produced by this experimental method with the limited amount of vapor pressure data on dioxins and furans which has previously been published. Schroy *et al.* (1985) has reported a 30°C solid vapor pressure for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin of 3.5×10^{-9} torr. When the vapor pressure calculated by this experiment is converted to a solid vapor pressure at 25°C via equation 1-2, the result is 1.0×10^{-9} torr, which compares quite favorably given the lower temperature.

The only other reported data is that of Rordorf (1985, 1987, and 1988), who measured, by the gas saturation method, the solid vapor pressures of 10 PCDD and 4 PCDF congeners and then used these data to predict the vapor pressures of an additional 15 dioxin and 51 furan congeners. These data have been compared to the current work by predicting the vapor pressure of each congener Rordorf studied with equation 3-4 and then converting them to solid-phase vapor pressures by equation 1-2 using the melting point data given by Rordorf. Figure 3-2 shows a log-log plot of this comparison with the regression line and the $y = x$ line. Although the results are well correlated ($r = 0.98$), the paired t-test shows that the data are different. The slope of the regression line is 1.21 ± 0.03, which indicates that the more chlorinated congeners show a greater vapor pressure than predicted by Rordorf, and the less chlorinated congeners show a lower vapor pressure than

Table 3-2. Measured isothermal gas chromatographic retention times, in minutes[a]

Dioxins

Temp ^{o}C	p,p-DDT	2378	12378	123478	1234678	12346789
90	19.0	14.1	42.23	110.5	280.45	654.0
100	9.13	7.00	19.82	48.86	120.86	269.6
110	4.50	3.61	9.73	23.10	55.18	118.5
120	2.37	1.97	5.05	11.45	26.20	55.48
130	1.32	1.13	2.72	5.95	13.07	22.66
140	0.76	0.67	1.54	3.22	6.89	13.58
150	0.48	0.44	0.92	1.83	3.78	7.25

Dibenzofurans

Temp ^{o}C	2378	12378	23478	123478& 123678	123789& 234678	1234678	1234789
90	19.05	12.45	27.96	37.44	75.9	100.6	180.0
100	9.08	6.22	13.50	17.62	34.91	45.90	80.22
110	4.51	3.23	6.81	8.68	16.86	21.76	37.17
120	2.37	1.76	3.60	4.51	8.49	10.83	18.15
130	1.31	1.02	2.00	2.46	4.53	5.69	9.35
140	0.75	0.60	1.15	1.40	2.51	3.07	5.00
150	0.46	0.38	0.69	0.82	1.45	1.73	2.78

[a] Denotes average of duplicate measurements.

Table 3-3. Regression parameters and experimental P_{gc} values

Compound	C^a	$L1/L2^a$	P_{gc} at 25°C (torr)	r^2
		Dioxins		
1234	0.011	0.952	7.83×10^{-7}	0.99
12378	-0.627	1.030	1.31×10^{-7}	0.90
123478	-1.223	1.090	2.97×10^{-8}	0.98
1234678	-1.865	1.138	7.68×10^{-9}	0.99
12346789	-2.388	1.191	2.08×10^{-9}	0.96
		Dibenzofurans		
2378	0.098	0.947	9.21×10^{-7}	0.99
12378	-0.436	0.993	2.73×10^{-7}	0.50^b
23478	-0.566	1.019	1.63×10^{-7}	0.88
123478& 123678	-1.084	1.051	6.07×10^{-8}	0.96
123789& 234678	-1.229	1.074	3.74×10^{-8}	0.97
1234678	-1.661	1.099	1.68×10^{-8}	0.99
1234789	-1.903	1.119	9.79×10^{-9}	0.99

[a] See equation 3-3.

[b] Removal of the 150°C data point improves r^2 to 0.95 but only causes a 5% change in P_{gc}.

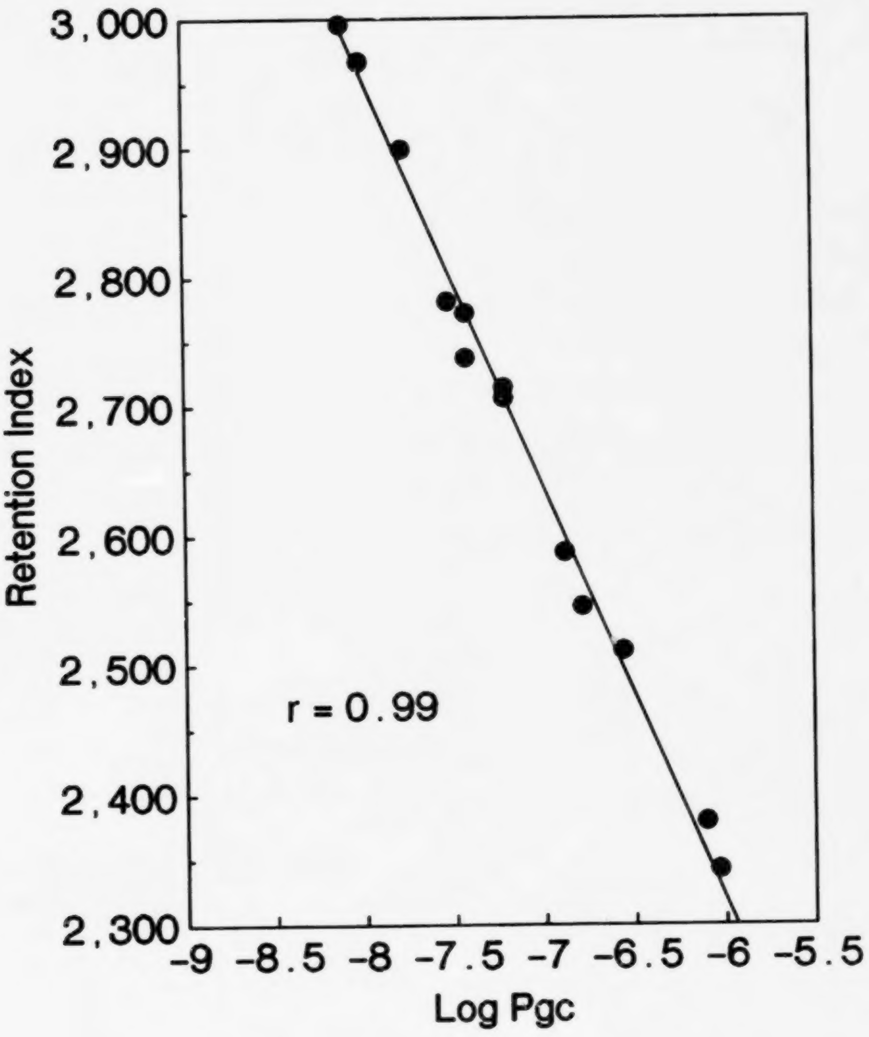


Figure 3-1. Plot of reported GC retention indexes *versus* experimental log(P_{gc}) values.

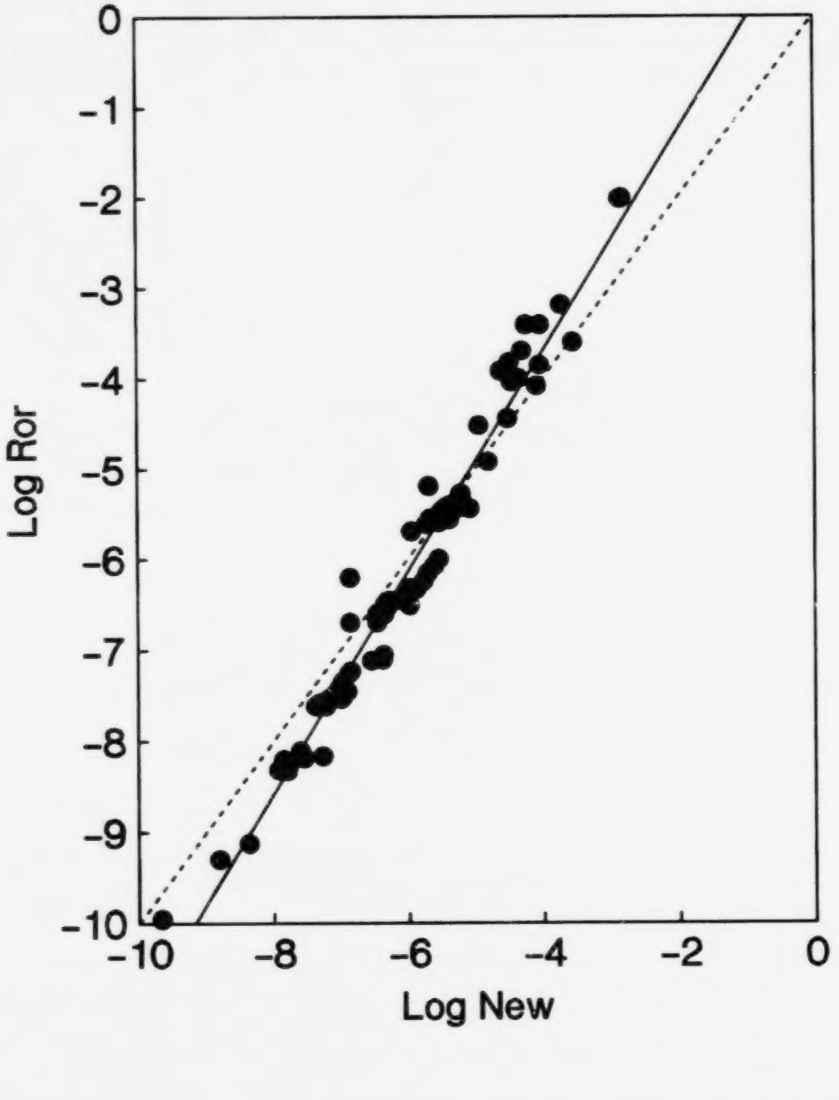


Figure 3-2. Plot of the solid-phase vapor pressures from Rordorf (1985, 1987, and 1988) *versus* this work. The regression line (solid) and the y=x line (dashed) are shown.

predicted by Rordorf. The worst outlier on this regression line is a point which represents 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Fortunately, Rordorf gives two different vapor pressures for this congener, and the other value agrees much better.

SUMMARY

We have predicted the vapor pressure of any PCDD/F congener or GC/MS peak in our database. The method predicts P_{gc}, which ranges from 10^{-6} torr for tetrachlorodioxins to 10^{-9} torr for octachlorodioxin. The good agreement with the literature's solid-phase vapor pressure values gives us confidence that P_{gc} is a reliable estimate of the sub-cooled liquid vapor pressure (P^l_o). Thus, for the remainder of this report, the vapor pressure values determined by this experiment will be considered the P^l_o value.

CHAPTER 4

PCDD AND PCDF IN THE AMBIENT ATMOSPHERE OF BLOOMINGTON, INDIANA

INTRODUCTION

As discussed in Chapter 1, PCDD and PCDF are injected into the atmosphere by various combustion processes and dispersed through the environment by atmospheric transport (Czuczwa *et al.*, 1984). These combustion processes produce a varying mixture of homologues and isomers, depending on fuel composition and combustion temperature. This varying mixture in the sources changes to a uniform distribution in the sinks during the atmospheric transport and depositional processes (see Chapter 1 and Czuczwa and Hites, 1986). Because of the varying toxicities of the PCDD/F congeners, it is important to understand the processes and parameters which control the rate at which individual congeners undergo these transformations.

As a first step in developing this understanding, it is important to measure the concentrations of PCDD/F in the ambient atmosphere. We chose Bloomington, Indiana, because of the proposed construction of an incinerator which would burn PCB-contaminated material along with the town's municipal waste. Given previous evidence on the production of PCDD/F in municipal incinerators (Buser and Bosshardt, 1978; Bumb *et al.*, 1980; Lustenhouwer *et al.*, 1980; Cavallaro *et al.*, 1982; Liberti and Brocco, 1982; Liberti *et al.*, 1982; Olie *et al.*, 1982; Rappe *et al.*, 1983, 1985, 1986; Tong and Karasek, 1986; Yasuhara *et al.*, 1987; Clement *et al.*, 1988) and in PCB fires (Rappe *et al.*, 1983 and 1985), this proposed incinerator could have a significant impact on Bloomington's air quality. Thus, this study also provides baseline data against which the impact of this incinerator on local PCDD/F concentrations could be judged. Measurements at the four locations (see Figure 2-1) over a 3-year period allowed small-scale local effects to be minimized and the primary sources of variability to be determined.

BLOOMINGTON AIR DATA

Our sampling system defines the two phases: Any compounds found on the glass fiber filter (GFF) are considered particle-bound, and those found on the polyurethane foam plug (PUF) are considered vapor phase. This definition has some caveats: **(a)** particles smaller than 0.1 μm might pass through the GFF and be absorbed by the PUF; **(b)** temperature changes during sampling, which can be quite large over a 3-day period, can cause particle-bound material on the GFF to vaporize and be "blown-off" to the PUF plug (Bidleman and Foreman, 1987); and **(c)** at large sample volumes, there is the potential of sample breakthrough on the PUF plug; however, our experiments showed that this did not occur for PCDD/F at the volumes we sampled.

As discussed in Chapter 2, the same peaks were consistently seen in each sample. Furthermore, the relative intensities of these peaks (within a homologue) were approximately the same from sample to sample. Thus, a standard GC/MS peak profile pattern for each homologue could be created. For example, Figure 4-1 shows these patterns for the hexachloro-dioxins (left) and furans (right). The bar heights are the geometric average relative intensities of the 95 Bloomington air samples (normalized to D6-3 and F6-6), and the error indicators on these bars are the upper geometric standard deviation of these averages. Note how small the error bars are. This indicates the consistency of the patterns. The normalized profiles show slight but systematic differences between the vapor and particle-bound phases. The cause of these differences will be discussed later.

Site Comparisons

At the homologue level, the four sites which were sampled showed relatively few differences. This can be seen in Figure 4-2, which plots geometric average homologue profiles for each of the four sites in both phases. Note that all sites show the same homologue profile: The total (vapor plus particle) concentrations of the furans always decrease with increasing degree of chlorination, while the dioxin concentrations always increase with degree of chlorination. All sites show that the less chlorinated homologues have a higher vapor phase fraction than the more chlorinated homologues. In addition, all sites show octachlorodioxin to be the most concentrated homologue, averaging from 440 to 690 fg/m^3. The average ratios of total particle-bound concentration to the TSP concentration for the Batchelor, Sanders, and Courthouse sites, were 31, 30, and 30 fg/μg, respectively. (TSP was not measured at SPEA.) Thus, small concentration differences which exist between the sites can be explained by TSP concentration differences.

The lack of major differences between the four sites indicates that there is no large local source which would have a greater impact on one particular site. Thus, the dioxins and furans found in Bloomington's ambient air are either from multiple small local sources [such as automobile exhaust (Ballschmiter *et al.*, 1986; Marklund *et al.*, 1987)] or from a few large, distant sources. In either case, the samples probably come from the same population and have, therefore, been averaged together for further analysis. These averages are presented in Table 4-1. This table gives the geometric average concentration of each peak in both the vapor (V) and particle-bound (P) phases (individual sample data from which these averages are obtained are given in the Appendix), the best estimate of the congeners present in the peak, and the peak's sub-cooled liquid vapor pressure (as estimated from equation 3-5). Summed averages for each homologue are also presented.

Temporal Effects

The temporal profiles for the total concentration (vapor plus particle-bound) of each homologue is shown in Figure 4-3. Note that the lines remain essentially parallel. Therefore, while the total concentrations changed, the relative amount of the different homologues did not. This indicates that the homologue concentrations do not appear to be affected by season. The variability in the total concentrations is shown in Figure 4-4, which plots the average atmospheric temperature during sampling against total PCDD/F concentration in that sample. The geometric mean of these data is 2.5 pg/m^3, with a geometric standard deviation range from 1.4 to 4.4 pg/m^3. Note that the correlation coefficient (r) was only 0.17; this is not significant for 95 measurements. This may indicate that heating fuels are not a major source of these compounds to the ambient atmosphere. Other sources

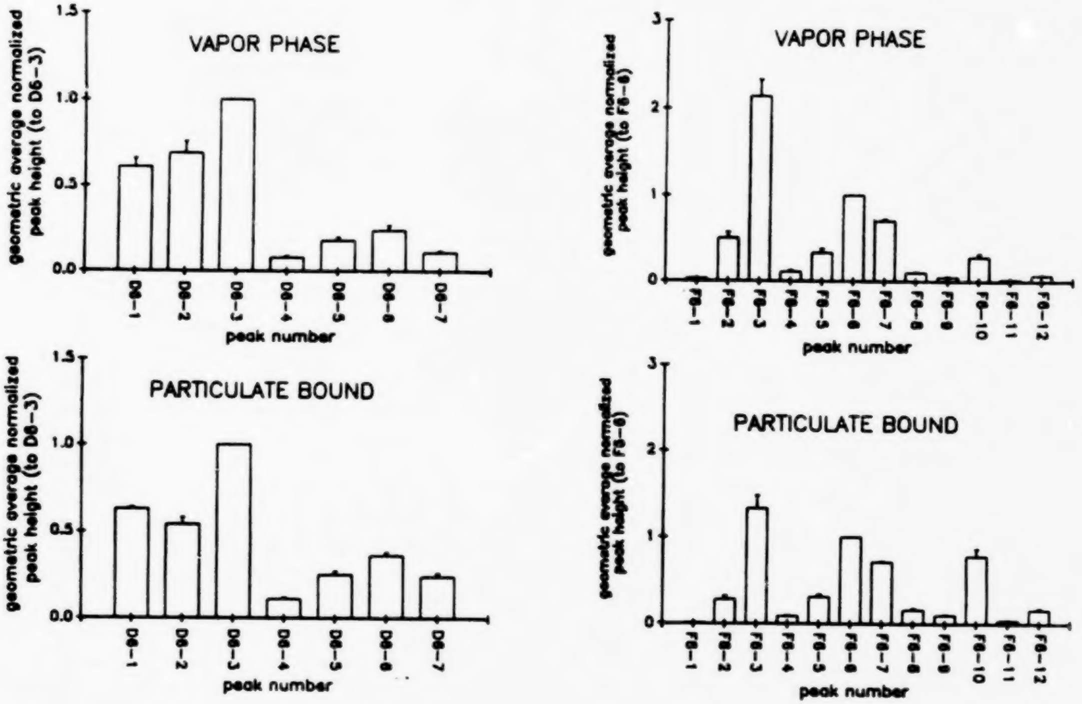


Figure 4-1. Average concentrations of the hexachlorodioxin (left) and hexachlorofuran peaks (right). Dioxin peaks are normalized to peak D6-3 in both the vapor phase (top) and particles (bottom). The best-estimate congener identifications for these peaks are: D6-1, 124679/124689; D6-2, 123468; D6-3, 123689/123679; D6-4, 123469; D6-5, 123478; D6-6, 123678; D6-7, 123789/123467. Furan peaks are normalized to F6-6 in both the vapor phase (top) and particles (bottom). The best estimate congener identifications for these peaks are: F6-1, 123468; F6-2, 134678/124678; F6-3, 134679; F6-4, 124679; F6-5, 124689; F6-6, 123478/123467; F6-7, 123678/123479; F6-8, 123679; F6-9, 123689/123469; F6-10, 234678; F6-11, 123789; F6-12, 123489.

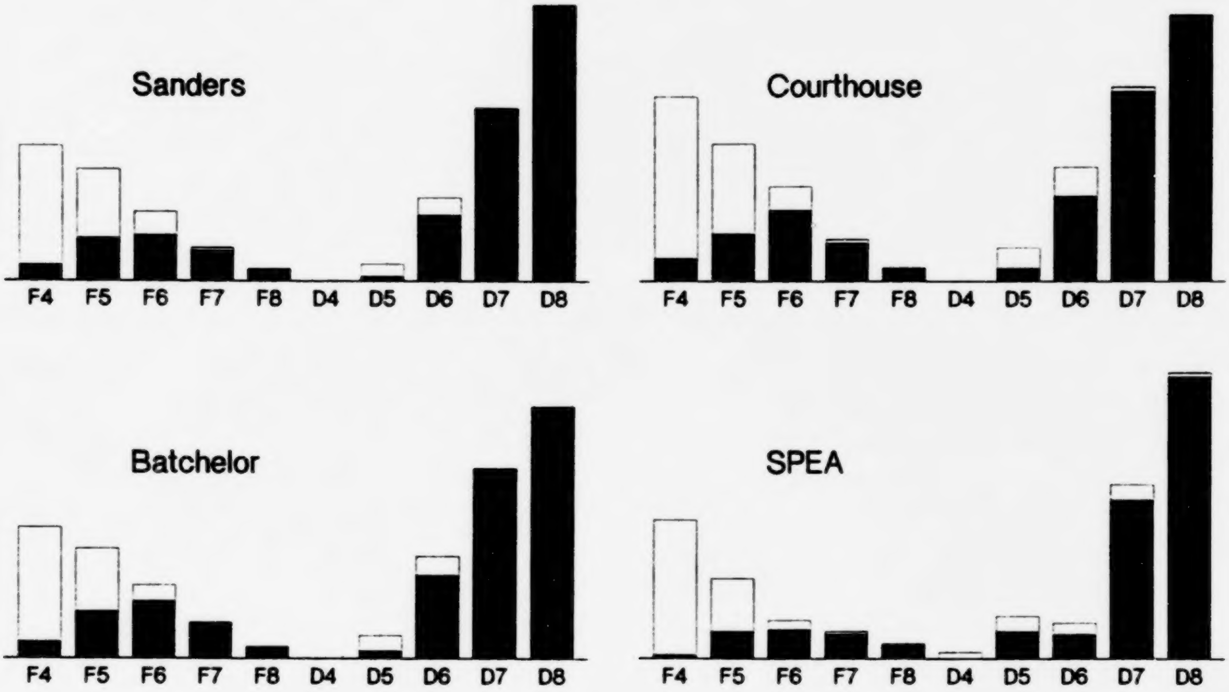


Figure 4-2. Homologue profiles showing the geometric average concentration for each homologue of the tetra-, penta-, hexa-, hepta-, and octachlorodibenzofurans (F4, F5, F6, F7, and F8, respectively) and tetra-, penta-, hexa-, hepta-, and octachlorodioxins (D4, D5, D6, D7, and D8, respectively) in both phases. The total (vapor plus particle-bound) D8 concentrations are: Sanders, 580 fg/m^3; Courthouse, 560 fg/m^3; Batchelor, 440 fg/m^3; SPEA, 690 fg/m^3. These values can be used as scale factor for each plot.

Table 4-1. Average vapor and particle-bound concentrations of GC/MS peaks.[a]

Peak	Congeners	Index	V (fg/m^3)	P (fg/m^3)	$-\log P_o^L$ (torr)
F4-1		2259	9.3	0.2	5.77
F4-2		2267	18	0.8	5.79
F4-3		2277	18	0.9	5.82
F4-4		2280	14	0.6	5.83
F4-5		2287	16	1.2	5.86
F4-6		2310	23	1.7	5.94
F4-7		2319	37	2.3	5.96
F4-8		2323	44	4.6	5.98
F4-9	1278	2332	7.6	1.2	6.01
F4-10		2344	3.2	0.8	6.05
F4-11	2378/2348/2346*	2351	41	7.0	6.07
F4-12		2365	7.4	1.0	6.12
F4-13		2372	3.9	0.6	6.14
Total tetrafurans			240	23	
Total tetradioxins			1.3	0.2	
F5-1	13468*	2425	1.6	0.4	6.32
F5-2	12468*	2429	2.1	0.3	6.33
F5-3		2468	1.4	0.6	6.46
F5-4		2474	32	13	6.48
F5-5		2481	9.3	4.1	6.50
F5-6		2499	24	15	6.56
F5-7	13469*	2510	8.6	4.8	6.60
F5-8	12378/12348*	2514	11	6.0	6.61
F5-9	23489*/12379*	2521	6.2	3.7	6.63
F5-10	13489*	2528	9.9	5.6	6.66
F5-11	23478/12369*	2552	8.3	8.2	6.74
F5-12	23467*/12489*	2557	10	11	6.75
F5-13	12349*	2571	1.1	1.2	6.80
Total pentafurans			126	74	
D5-1	12468/12479	2484	10	4.1	6.51
D5-2	12469*	2502	1.3	0.7	6.57
D5-3	12368*	2515	8.2	3.9	6.61
D5-4	12478*	2522	0.6	0.4	6.63
D5-5	12379*	2531	1.5	0.9	6.67
D5-6	12369*/12467*/12489*	2544	0.9	0.7	6.71
D5-7	12347/12346*	2553	3.0	1.7	6.74
D5-8	12378	2570	0.4	0.5	6.80
D5-9	12367*	2585	0.2	0.2	6.85
D5-10	12389	2596	0.1	0.1	6.95

(continued)

[a] List of peaks measured, known, or best estimate of congeners included in peak, retention index, geometric average concentrations of the vapor (V) and particle-bound (P) phases, and the sub-cooled liquid vapor pressure at 25°C. Congeners labeled with an asterisk are best estimates and might be present in the preceding or following peak. Congeners underlined are the more toxic congeners, members of the so-called "dirty dozen." Peaks with no congeners specified could not be precisely matched to a specific congener.

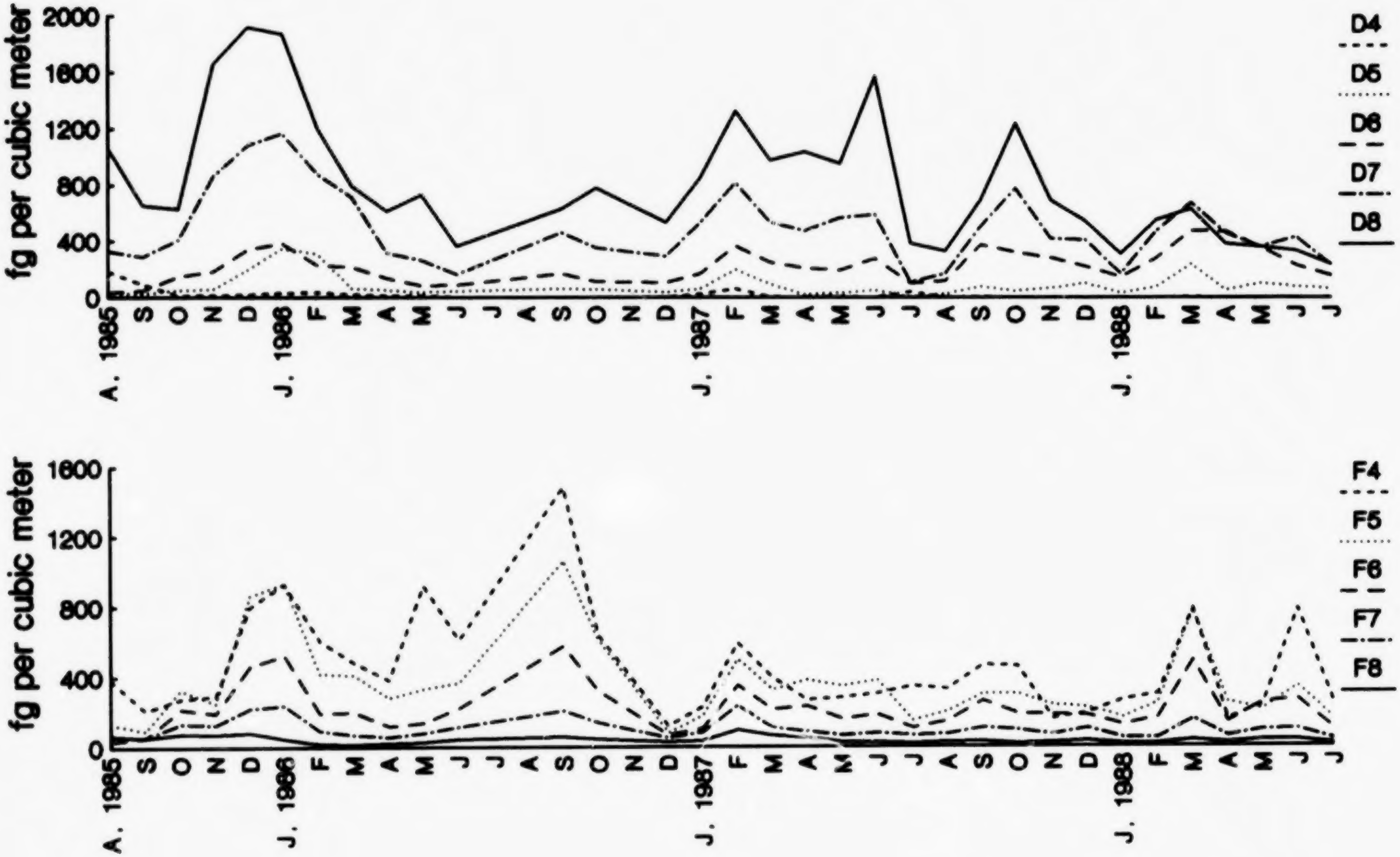


Figure 4-3. Monthly average total (vapor plus particle-bound) concentrations of each homologue. Samples prior to September 1986 were taken only at the SPEA sampling site.

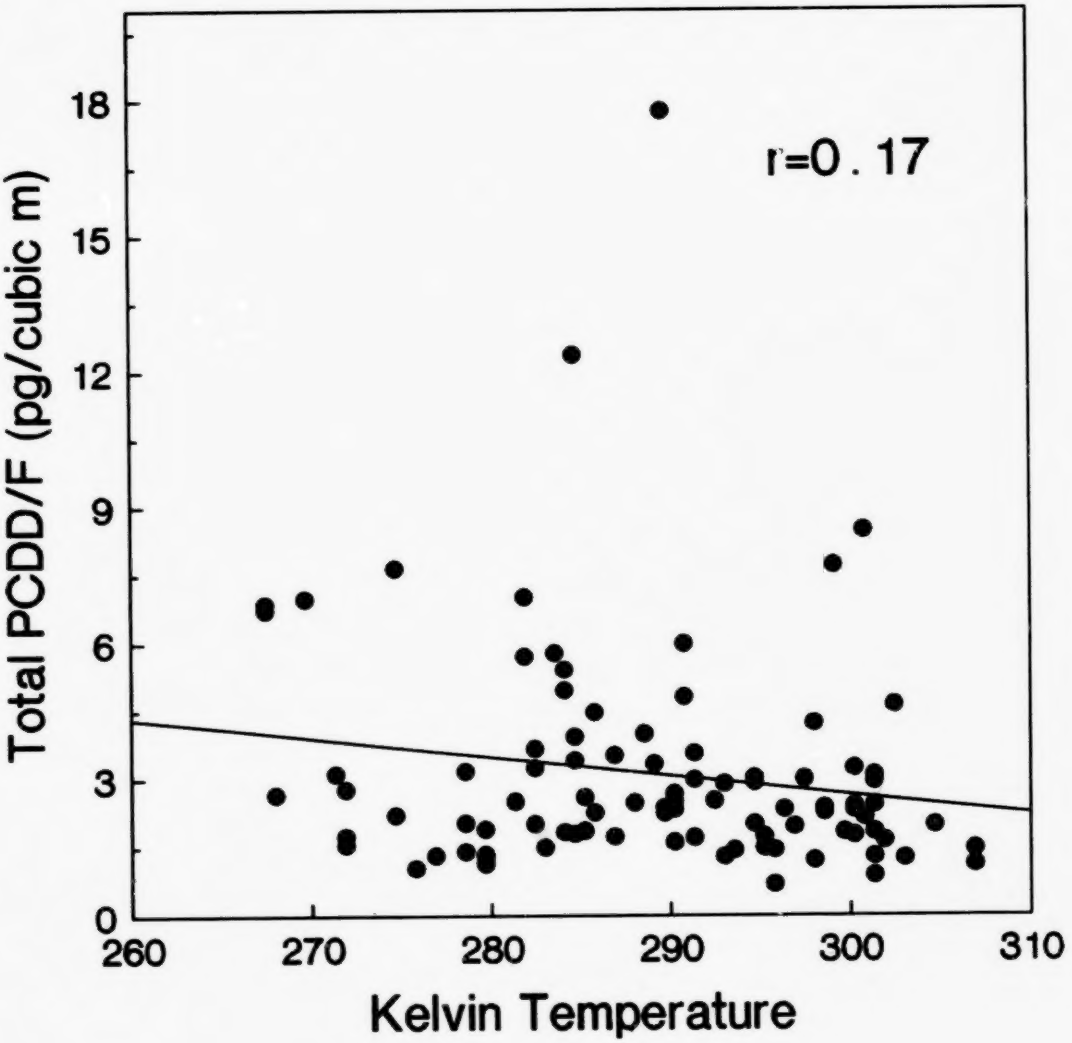


Figure 4-4. Total PCDD/F concentration *versus* Kelvin temperature. The correlation is not significant.

which do not have a seasonal component, such as waste incineration or automobile exhaust are not ruled out.

ATMOSPHERIC TEMPERATURE EFFECTS

Although there is no seasonal effect on the total concentrations, there is one on the proportion of the total atmospheric burden present in the vapor phase. During the warm summer months, the total vapor-to-particle-bound ratio (V/P) can be as great as 2, while in the winter, it can be less than 0.5. Figure 4-5 shows the effect of temperature on the homologue profiles. At warm temperatures (bottom), most of the less chlorinated homologues are found in the vapor phase, while at cooler temperatures (top) the burden is split between the two phases. The more chlorinated homologues are primarily present as particle-bound material even at the higher temperatures. To examine this effect in more detail, it is necessary to understand the effects of temperature and vapor pressure on the process of V/P partitioning.

Vapor-to-Particle Partitioning

Two models have been used to describe the partitioning of semivolatile organic compounds in air. The theoretically based model of Junge (1977) was discussed in Chapter 1. There is also an experimentally defined model developed by Yamasaki *et al.* (1982) and Bidleman and Foreman (1987). The theoretical model is based on adsorption theory; its important parameters are the particle surface area per cubic meter of air, the saturation vapor pressure of the compound, and the heat of condensation. The experimental model uses TSP concentration and temperature; from it, heats of adsorption can be determined. Pankow *et al.* (1984) gives a detailed discussion of the two models and shows that the Clausius-Clapeyron equation makes the two models equivalent. From these models, it seems clear that the primary determinant of an individual congener's V/P ratio is the compound's vapor pressure. In fact, Bidleman and Foreman (1987) have shown that at constant temperature and TSP concentrations

$$\log(V/P) = \log P^{l}_{0} + a_{0} \tag{4-1}$$

where a_0 is a constant depending on the units of P^{l}_{0}, the sub-cooled liquid vapor pressure of the compound. The slope of 1 indicates that V/P is directly proportional to vapor pressure.

An average V/P ratio for each of the measured peaks was calculated by dividing the average vapor concentration by the average particle-bound concentration for each peak (from Table 4-1). This averaging eliminated the effects of varying atmospheric temperatures and TSP concentrations, which we will discuss later. This V/P ratio is plotted against sub-cooled liquid vapor pressure in Figure 4-6. The strong effect of vapor pressure on V/P partitioning is apparent. The regression is excellent ($r = 0.96$), and the slope is close to unity (1.15), as predicted from equation 4-1. The V/P ratio ranges from 0.01 to 30; this is in good agreement with the theoretical model's prediction of V/P ratios between 0.05 and 100 for compounds with vapor pressures equal to those given here (Junge, 1977; Chapter 1). It is interesting to note that the vapor pressure's effect on V/P partitioning also manifests itself on the pattern of peaks within a given homologue. As shown earlier in Figure 4-1, the peak profiles were slightly different between the two phases; as

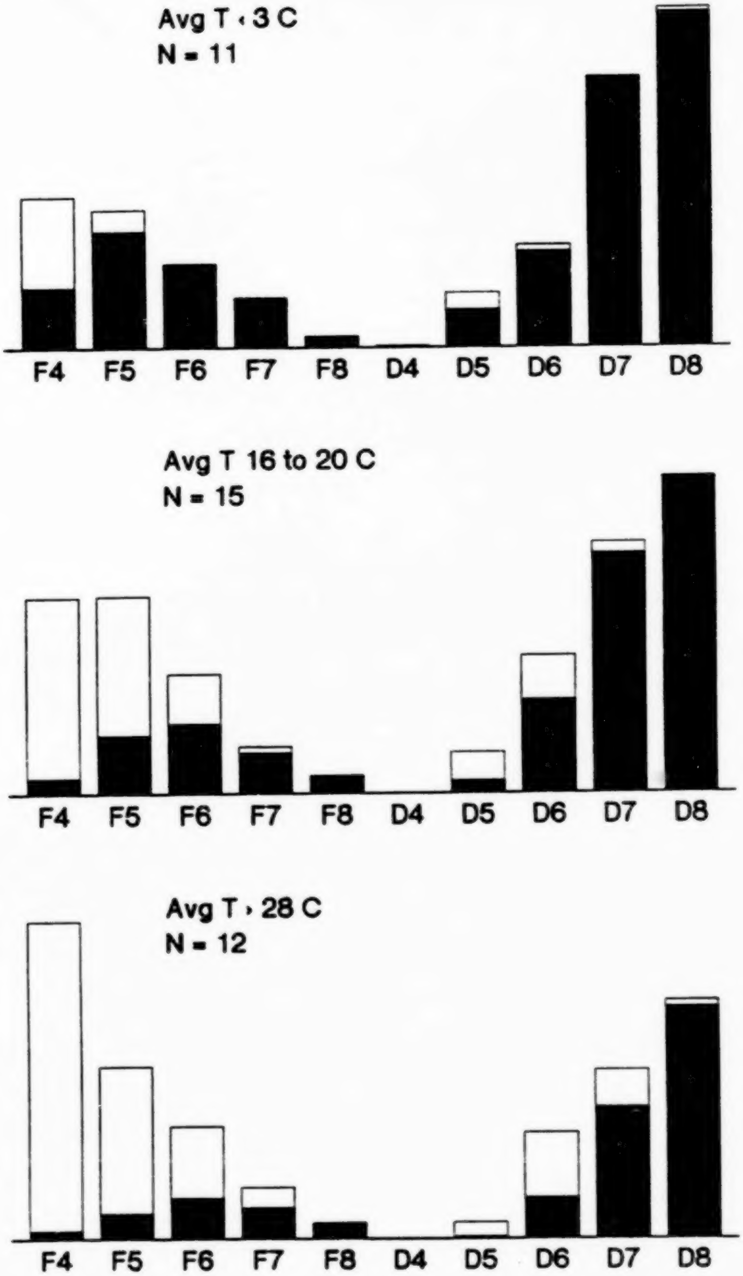


Figure 4-5. Homologue profiles for all samples taken during three average temperature ranges.

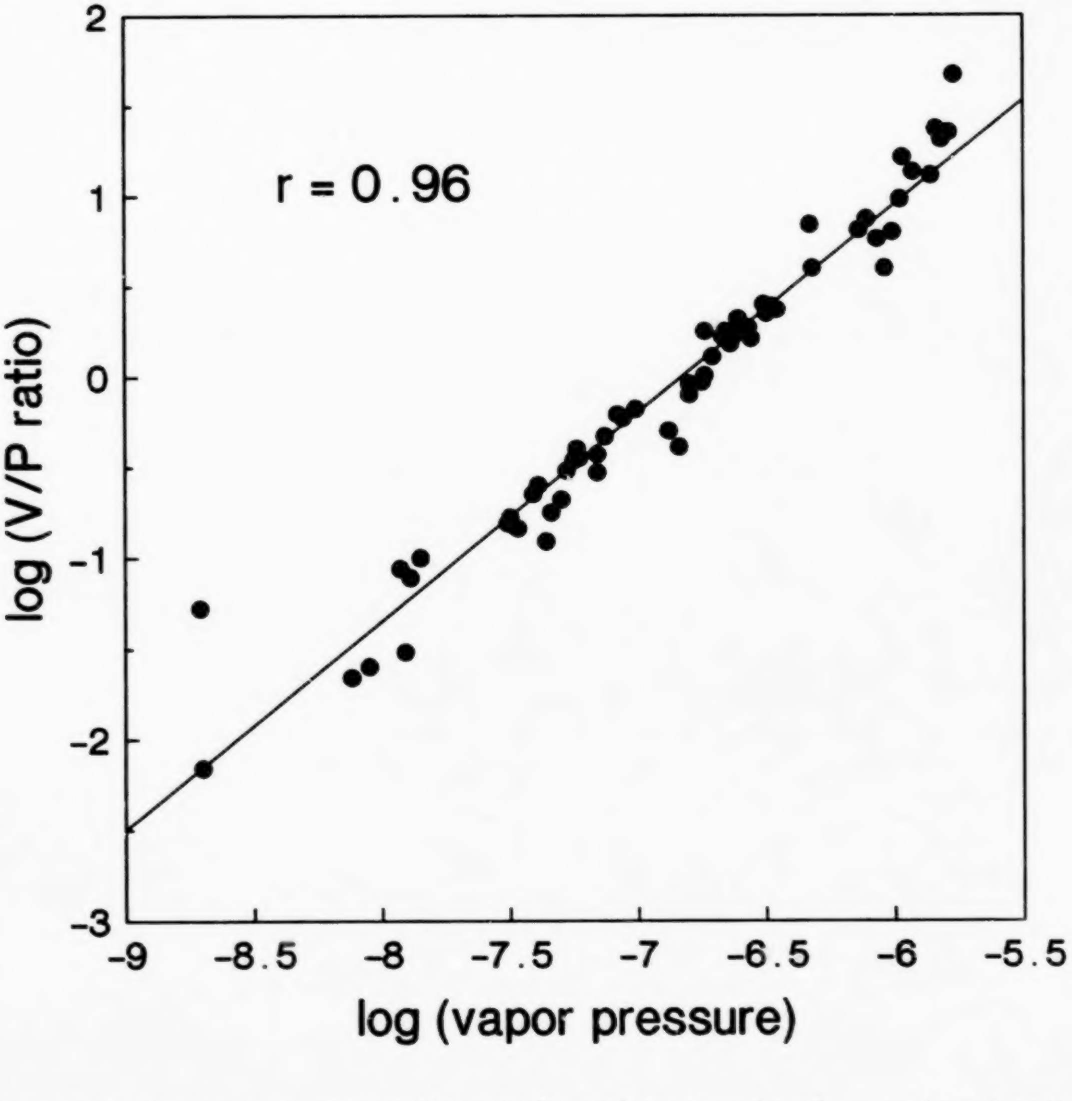


Figure 4-6. Average vapor-to-particle ratio for each measured peak *versus* its sub-cooled liquid vapor pressure.

expected, the later eluting GC/MS peaks (the congeners with the lower vapor pressure) are relatively more abundant in the particle-bound phase.

Vapor pressure is a strong function of temperature; thus, the V/P ratio should depend on the ambient atmospheric temperature. Yamasaki *et al.* (1982) and Bidelman and Foreman (1987) addressed this issue when they developed their experimentally defined model; their model states

$$\log [V(TSP)/P] = a'_0 + a_1/T \qquad (4\text{-}2)$$

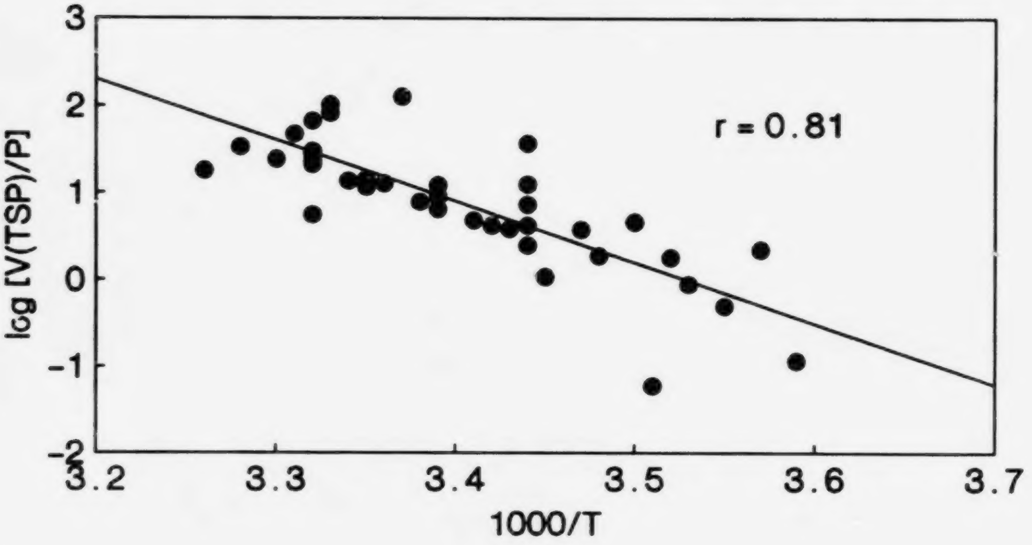
where a'_0 and a_1 are determined by regression of the experimental data. We applied this model to our data set, and for each peak, we carried out a regression analysis using equation 4-2. Examples of these regressions are shown in Figure 4-7 for 1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin (top) and 1,2,3,4,6,7,8-heptachlorodibenzofuran (bottom). The regression parameters for each of the GC/MS peaks analyzed are presented in Table 4-2. The various regressions were based on different numbers of data points, because only samples with detectable vapor and particle concentrations for a given GC/MS peak were used for that GC/MS peak. In addition, these regressions assumed a constant temperature over the 2- to 3-day sampling period and neglected errors associated with "blow-off" (Bidleman and Foreman, 1987) or with PCDD/F irreversibly adsorbed to the particles (Townsend *et al.*, 1987). Given these large potential error sources, the amount of scatter about the regression lines is quite acceptable. In fact, with the exception of seven GC/MS peaks, all peaks showed correlations that were significant at the 98% significance level or better. The peaks which did not reach this confidence level were generally those of minor components (such as D5-9); therefore, they had fewer measurements in which both vapor and particle components were present at detectable levels.

Heats of Adsorption

The good correlations seen in these regressions allowed us to estimate the heats of adsorption for these compounds. The Clausius-Clapeyron equation predicts that

$$H_A = 2.303\, R\, a_1 \qquad (4\text{-}3)$$

where H_A is the heat of adsorption; R is the gas constant; and a_1 is the slope from the equation 4-2 regression. The error sources discussed previously cause considerable scatter about the regression lines; thus, these heat-of-adsorption values are only estimates. Measured heats of adsorption ranged from -10 to -32 kcal/mole (omitting the nonsignificant values). These values are similar to those Foreman and Bidleman (1985) calculated for several semivolatile organochlorines by the same approach. The heats of adsorption tend to increase as the vapor pressure decreases ($r = 0.40$ for the dioxins and $r = 0.57$ for the furans), or correspondingly, as the degree of chlorination increases. This indicates that the V/P ratio for the more chlorinated congeners has a greater temperature dependence than do the less chlorinated congeners.



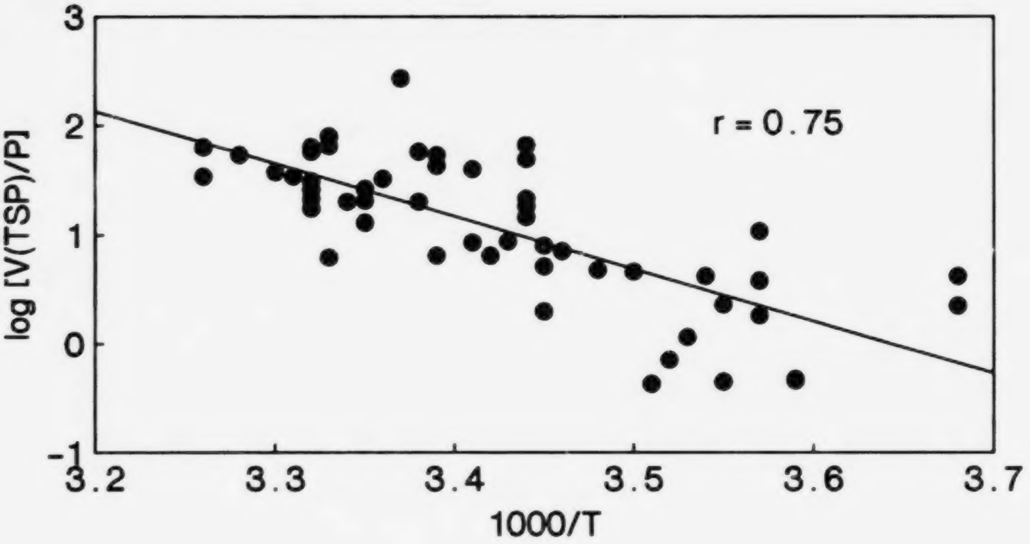


Figure 4-7. Plots of log[vapor(TSP)/particle] *versus* reciprocal temperature for GC/MS peak D7-1, 1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin (top) and GC/MS peak F7-1, 1,2,3,4,6,7,8-heptachlorodibenzofuran (bottom).

Table 4-2. Vapor particle partitioning regression parameters.[a]

Peak	a_1	a'_o	n	r^2	Prob>F	H_a (Kcal/mole)
F4-1	-4660	18.8	25	0.45	0.0002	-21.3
F4-2	-2790	12.0	36	0.28	0.0007	-12.8
F4-3	-3490	14.6	37	0.53	0.0001	-15.9
F4-4	-3600	15.0	36	0.51	0.0001	-16.5
F4-5	-3370	14.2	36	0.54	0.0001	-15.4
F4-6	-3440	14.4	52	0.37	0.0001	-15.7
F4-7	-4040	16.5	51	0.48	0.0001	-18.5
F4-8	-2720	11.8	56	0.39	0.0001	-12.4
F4-9	-2350	10.4	47	0.31	0.0001	-10.7
F4-10	-2710	11.5	41	0.26	0.0005	-12.4
F4-11	-2570	11.0	57	0.34	0.0001	-11.7
F4-12	-3170	13.2	45	0.42	0.0001	-14.5
F4-13	-3600	14.6	38	0.44	0.0001	-16.4
F5-1	-2710	11.6	38	0.25	0.0013	-12.4
F5-2	-2470	11.0	36	0.23	0.0026	-11.3
F5-3	-2780	11.6	29	0.37	0.0003	-12.7
F5-4	-4100	16.2	57	0.75	0.0001	-18.7
F5-5	-3990	15.8	56	0.67	0.0001	-18.2
F5-6	-4140	16.2	60	0.78	0.0001	-18.9
F5-7	-3720	14.8	60	0.69	0.0001	-17.0
F5-8	-3940	15.5	60	0.68	0.0001	-18.0
F5-9	-3790	15.0	58	0.61	0.0001	-17.3
F5-10	-4350	16.9	59	0.67	0.0001	-19.9
F5-11	-3940	15.2	60	0.66	0.0001	-18.0
F5-12	-4720	17.9	60	0.77	0.0001	-21.6
F5-13	-3650	14.4	40	0.52	0.0001	-16.7
D5-1	-3340	13.5	54	0.44	0.0001	-15.3
D5-2	-3740	14.7	37	0.36	0.0001	-17.1
D5-3	-2390	10.1	54	0.33	0.0001	-10.9
D5-4	-1470	6.9	27	0.09	0.1195	-6.7
D5-5	-2280	9.7	37	0.21	0.0046	-10.4
D5-6	-3860	15.0	35	0.50	0.0001	-17.6
D5-7	-2050	8.9	42	0.30	0.0001	-9.4
D5-8	-3150	12.6	25	0.31	0.0029	-14.3
D5-9	-740	4.4	10	0.01	0.7368	-3.4
D5-10	-1420	6.6	3	0.04	0.8031	-6.5

(continued)

Peak	a_1	a'_o	n	r^2	Prob>F	H_a (Kcal/mole)
F6-1	-2200	9.3	13	0.17	0.1492	-10.1
F6-2	-4460	16.9	45	0.58	0.0001	-20.4
F6-3	-4780	18.0	57	0.73	0.0001	-21.8
F6-4	-4610	17.4	38	0.48	0.0001	-21.1
F6-5	-4440	16.8	45	0.68	0.0001	-20.3
F6-6	-4340	16.3	58	0.63	0.0001	-19.8
F6-7	-3970	15.1	57	0.62	0.0001	-18.1
F6-8	-3640	13.9	39	0.60	0.0001	-16.6
F6-9	-3720	14.2	35	0.56	0.0001	-17.0
F6-10	-4380	16.2	50	0.61	0.0001	-20.0
F6-11	-1400	6.2	23	0.21	0.0258	-6.4
F6-12	-2120	8.6	36	0.26	0.0014	-9.7
D6-1	-6050	22.1	56	0.78	0.0001	-27.6
D6-2	-4960	18.5	54	0.66	0.0001	-22.7
D6-3	-4490	16.8	57	0.66	0.0001	-20.5
D6-4	-4160	15.7	40	0.47	0.0001	-19.0
D6-5	-2790	10.9	52	0.38	0.0001	-12.8
D6-6	-3970	15.0	52	0.59	0.0001	-18.1
D6-7	-3880	14.5	47	0.48	0.0001	-17.7
F7-1	-4790	17.5	52	0.56	0.0001	-21.9
F7-2	-6610	23.6	23	0.56	0.0001	-30.2
F7-3	-5140	18.6	48	0.68	0.0001	-23.5
F7-4	-2280	8.8	20	0.21	0.0382	-10.4
D7-1	-6990	24.7	40	0.64	0.0001	-31.9
D7-2	-6100	21.6	39	0.60	0.0001	-27.9
F8	-1150	4.8	38	0.06	0.1499	-5.3
D8	-3250	11.4	30	0.29	0.0018	-14.9

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[a] See equation 4-2. Shown are the peak identifier, a_1, a'_o, number of samples used in the regression (n), r^2 for the regression, the probability that a greater F statistic would occur by chance, and the heat of adsorption.

SUMMARY

To summarize, our data have shown that the two key parameters controlling the phase in which a particular congener is found in the atmosphere are the ambient temperature and that congener's vapor pressure. Because the less chlorinated congeners have higher vapor pressures, they are found to a greater extent in the vapor phase. Obviously, this has implications on the atmospheric transport process and on the ultimate environmental fate of these compounds; for example, photodegradation will proceed at different rates for the different phases. Thus, depending on the process involved and the ambient temperature, there will be differences in the atmospheric behavior of the various PCDD and PCDF.

CHAPTER 5

TRANSPORT AND DEPOSITION OF PCDD/F

PCDD/F are produced by combustion processes such as waste incineration (see Chapter 1). Once produced, these compounds are injected into the atmosphere, where they can be transported long distances before they are deposited (Czuczwa *et al.*, 1984). Because of the high toxicity of some of the individual PCDD/F congeners, it is important to understand the transformations which these compounds might undergo during the transport and depositional processes.

It is known that transformations are occurring. For example, there are noticeable changes in the homologue profile (Czuczwa, 1984; Czuczwa and Hites, 1986; Chapter 1). Combustion sources show a large range in concentrations and relative amounts of the various homologues; even a single source will show changes with fuel and with combustion temperature (Clement *et al.*, 1988). Conversely, sediment samples (the ultimate environmental sink) consistently show the same relative amounts of the various homologues (Czuczwa, 1984; Czuczwa and Hites, 1986). Though there is clear evidence that there are transformations occurring during transport and deposition, we do not fully understand the processes causing these transformations.

Our understanding of these processes is limited by our lack of information on PCDD/F concentrations in the environmental compartments which link the combustion sources to the sedimentary sinks. These compartments are ambient air and rain. Furthermore, PCDD/F can be present in various phases in each compartment: they can be found in particle-bound and vapor phases in air and in particle-bound and dissolved phases in rain. These phases will interact with each other and undergo degradation processes (such as photodegradation) at different rates.

This chapter reports on the depositional processes. Thus, it examines the interaction between air and rain samples, assesses geographic variability, and explains the source-to-sink transformations.

PCDD/F IN BLOOMINGTON, INDIANA, RAIN

As mentioned previously in Chapter 2, the rain sampler was modified during the course of the study. The modification allowed the on-line filtration of rainwater samples as they were collected. Thus, our sample collection procedures defined our phases. Any material found on the filters was considered particle-bound; material found in the rainwater was considered dissolved. There are obviously some limitations: the PCDD/F in rainwater could dissolve from or adsorb to the filtered material.

Rain Concentrations

Concentrations for rain samples taken with on-line filtration were often close to detection limits, and thus, these samples were only analyzed by homologue classes. These data are presented in Table 5-1. Total concentrations range from 10 to 84 pg/L in the dissolved phase and 37 to 320 pg/L in the particle-bound material. Because of the closeness to the detection limits, the data set was of limited utility. Thus, only the average rain data will be considered for further analysis (geometric averages used the 0.1 pg/L detection limit for values which were not detected).

Rain Washout

The average concentrations of the tetra- through octachloro- homologues in each of the four phases for Bloomington air and rain are presented in Table 5-2. The less chlorinated homologues of both the dioxins and furans tend to have a greater proportion of their concentrations in the vapor and dissolved phases while the more chlorinated homologues tend to prefer the particle-bound phases. For example, the ratio of vapor-to-particle concentrations for the furans in air ranges from 10 for the tetrachloro- homologue down to 0.05 for the octachloro- homologue. The total concentrations (vapor-plus-particle for air or dissolved- plus-particle for rainwater) show the same trends in air and rainwater: The furans decrease in concentration with increasing level of chlorination while the dioxins increase in concentration with level of chlorination.

We can compare these air and rain concentrations to one another using the concept of washout (Bidleman, 1988). This is expressed as the ratio between the concentration in rain and the concentration in air on a volume-to-volume basis. This ratio, usually given the symbol W, is a measure of scavenging efficiency. As a rain event occurs, compounds are scavenged from the air and transferred into the rainwater. Depending on the intensity and duration of the rain event, the amount transferred from the air to the rain varies. As an example, consider the last three rain samples presented in Table 5-1. After 3 days of continuous rain, there was essentially no particles in the rainwater, and thus, no detectable PCDD/F on the filters. Nevertheless, during this event, all three samples of dissolved-phase showed PCDD/F. Clearly, the first and last of these three samples would show different washout values. (Note: the final sample was discarded for the particle-bound average.)

Washout measurements are highly variable (Ligocki *et al.*, 1985a and 1985b; Bidleman, 1988). Furthermore, they are ideally measured by determining the concentrations of the compound in air and rain samples taken simultaneously. We could not use this approach because the large sample volumes necessary for air measurements required us to sample for longer time periods than the duration of most rain events. We did, however, estimate washout by using the average concentrations measured in our ambient rain and air data (see Table 5-2).

There are two distinct and separate phenomena to be examined. Gas scavenging is the equilibrium process in which a compound partitions between vapor and aqueous phases; its measure is W_g, which is the ratio of the air vapor phase to rain dissolved-phase concentrations. Particle scavenging is the process by which rainfall removes particles and the compounds bound to those particles from the atmosphere; its measure is W_p, which is the ratio of the air particle phase to rain

Table 5-1. Concentration of PCDD and PCDF homologues for rain samples.[a]

Date	F4	F5	F6	F7	F8	D4	D5	D6	D7	D8	Total
Dissolved											
6/13/87	1.8	1.3	nd	0.2	0.4	nd	nd	nd	nd	19	23
6/14/87	3.8	1.8	nd	nd	nd	nd	nd	nd	nd	8.4	14
6/30/87	14	6.4	0.5	1.7	6.7	1.2	nd	nd	1.1	45	77
8/3/87	2.8	1.6	nd	nd	nd	nd	nd	nd	nd	5.5	11
10/28/87	1.9	1.0	0.3	0.9	0.6	nd	nd	2.2	9.4	46	62
3/27/88	6.3	8.2	nd	nd	0.7	nd	9.1	14	11	12	62
4/7/88	3.4	3.5	2.1	1.9	0.9	nd	nd	nd	8.8	34	55
5/24/88	nd	nd	nd	nd	nd	nd	nd	nd	nd	40	40
6/16/88	19	nd	nd	nd	nd	nd	nd	nd	nd	nd	19
7/11/88	9.3	nd	nd	nd	nd	nd	nd	nd	17	18	45
7/19/88	11	4.4	nd	nd	nd	nd	nd	nd	24	25	65
7/20/88a	3.7	1.7	1.0	0.5	0.3	nd	0.2	1.1	2	2.8	13
7/20/88b	9.4	1.5	1.2	nd	nd	nd	0.7	nd	5.5	5.0	24
7/21/88	19	5.4	2.1	7.8	5.2	nd	3.4	nd	23	18	84
Particle-bound											
6/13/87	0.5	1.0	1.0	1.7	0.5	nd	nd	0.4	13	54	72
6/14/87	1.2	2.7	1.7	3.2	1.4	nd	nd	1.3	15	92	120
6/30/87	nd	nd	nd	nd	nd	nd	nd	nd	5.6	49	55
8/3/87	0.3	1.0	0.7	1.0	nd	nd	nd	0.2	7.2	27	38
10/28/87	6.2	5.0	3.4	3.5	1.0	8.3	1.1	5.9	23	47	100
3/27/88	5.3	7.1	6.9	8.2	2.4	1.9	nd	11	56	220	320
4/7/88	5.3	17	14	10	2.1	nd	1.4	15	44	94	200
5/24/88	2.2	3.1	nd	nd	nd	nd	nd	nd	34	46	86
6/16/88	3.8	3.9	15	8.8	nd	nd	nd	16	38	48	130
7/11/88	5.1	5.3	nd	3.8	nd	nd	nd	nd	18	20	53
7/19/88	nd	nd	nd	4.4	nd	nd	nd	22	61	42	130
7/20/88a	1.7	2.5	2.0	3.4	1.6	nd	1.0	1.4	17	11	42
7/20/88b	0.6	nd	1.0	2.1	nd	nd	nd	1.6	22	12	40

[a] Units: pg/L; nd = not detected

Table 5-2. Average PCDD/F homologue concentrations for ambient air and rain samples taken in Bloomington, Indiana.

	Air		Rain	
Homologue	Vapor (fg/m^3)	Particle (fg/m^3)	Dissolved (pg/L)	Particle (pg/L)
F4	240	23	4.5	1.2
F5	130	74	1.3	1.5
F6	31	82	0.3	1.0
F7	5.8	65	0.3	2.1
F8	1.4	27	0.3	0.3
D4	1.3	0.2	0.1	0.2
D5	26	13	0.2	0.2
D6	33	120	0.2	1.4
D7	10	370	1.6	22
D8	4.1	590	11	43

particle phase concentrations. Our calculated W_g and W_p values are given in Table 5-3, second and third columns.

The differences between the two processes are demonstrated in Figure 5-1, which plots the washout ratios as a function of the homologue's average vapor pressure. Note the strong correlation for W_g (significant at the 1% level) and the lack of correlation for W_p. The latter indicates that particle washout is a physical process acting on the particle, and therefore, all of the compounds bound to the particle are affected similarly. Conversely, vapor washout appears to be highly dependent on the compound's vapor pressure; therefore, it must involve a different process than particle washout.

The vapor washout process involves the dissolution of the gas phase into water. If it is assumed that during rainfall, equilibrium is reached between the gas and dissolved phases [which Slinn *et al.* (1978) estimates to be the case], then W_g can be used to estimate the Henry's law constant (H) for a compound. This constant is the equilibrium ratio of a compound's vapor pressure to its water solubility at a given temperature. Thus, for gas scavenging, as shown by Ligocki *et al.* (1985a),

$$H = RT/W_g \tag{5-1}$$

where R is the gas constant and T is the absolute temperature. Vapor pressure and solubility are both temperature dependent variables, and thus, Henry's law constants show variations with temperature (Burkhard *et al.*, 1985). Because our average data cover a broad range of temperatures, our Henry's law constants can only be considered estimates. The Henry's law constants were calculated using an average temperature of 290 K and are given in the last column of Table 5-3. Shiu *et al.* (1988) reported that Henry's law constants for several PCDD ranged from 3.7×10^{-5} to 1.3×10^{-6} atm·m^3/mole, which compare quite favorably with our data. These estimated Henry's law constants are a factor of 10 to 100 lower than those measured for PCBs with the same number of chlorine atoms at 25°C (Burkhard *et al.*, 1985).

The measured particle scavenging ratios, presented in Table 5-3, are quite similar to those measured by Ligocki *et al.* (1985b) for semivolatile organic compounds, but they are lower than those reviewed by McMahon and Denison (1979) and Slinn *et al.* (1978). Lower particle scavenging ratios might reflect either below-cloud scavenging (Ligocki *et al.*, 1985b) or the possibility that PCDD and PCDF are associated with the smaller particles which are scavenged less efficiently (Slinn *et al.*, 1978; McVeety and Hites, 1988).

Total washout is given by (Ligocki *et al.*, 1985b; Bidleman, 1988):

$$W = W_g(1-p^\bullet) + W_p\, p^\bullet \tag{5-2}$$

where $p^\bullet$ is the fraction of the total air concentration which is bound to particles. Dividing $W_p p^\bullet$ by W allows us to determine which type of scavenging is the dominant process for a given compound. Total washout values and percent particle scavenging are presented in Table 5-3. These data are in the same range (though on the low side) as several experimental and predicted values for organochlorines as reviewed by Bidleman (1988).

Table 5-3. Washout estimates based on average Bloomington air and rain data.[a]

	Washout Ratio				-log H[b]
Homologue	Gas	Particle	Total	%P[c]	atm·m³/mole
F4	19000	52000	22000	21	4.87
F5	10000	20000	14000	54	4.62
F6	9700	12000	11000	77	4.61
F7	52000	32000	34000	88	5.34
F8	210000	11000	21000	52	5.95
D5	7700	15000	10000	50	4.51
D6	6100	12000	10000	88	4.41
D7	160000	59000	62000	93	5.83
D8	2700000	72000	90000	80	7.05

[a] The tetrachloro dioxin homologue is not listed because it was rarely detected.

[b] Henry's law constant.

[c] Percent washout due to the particle phase.

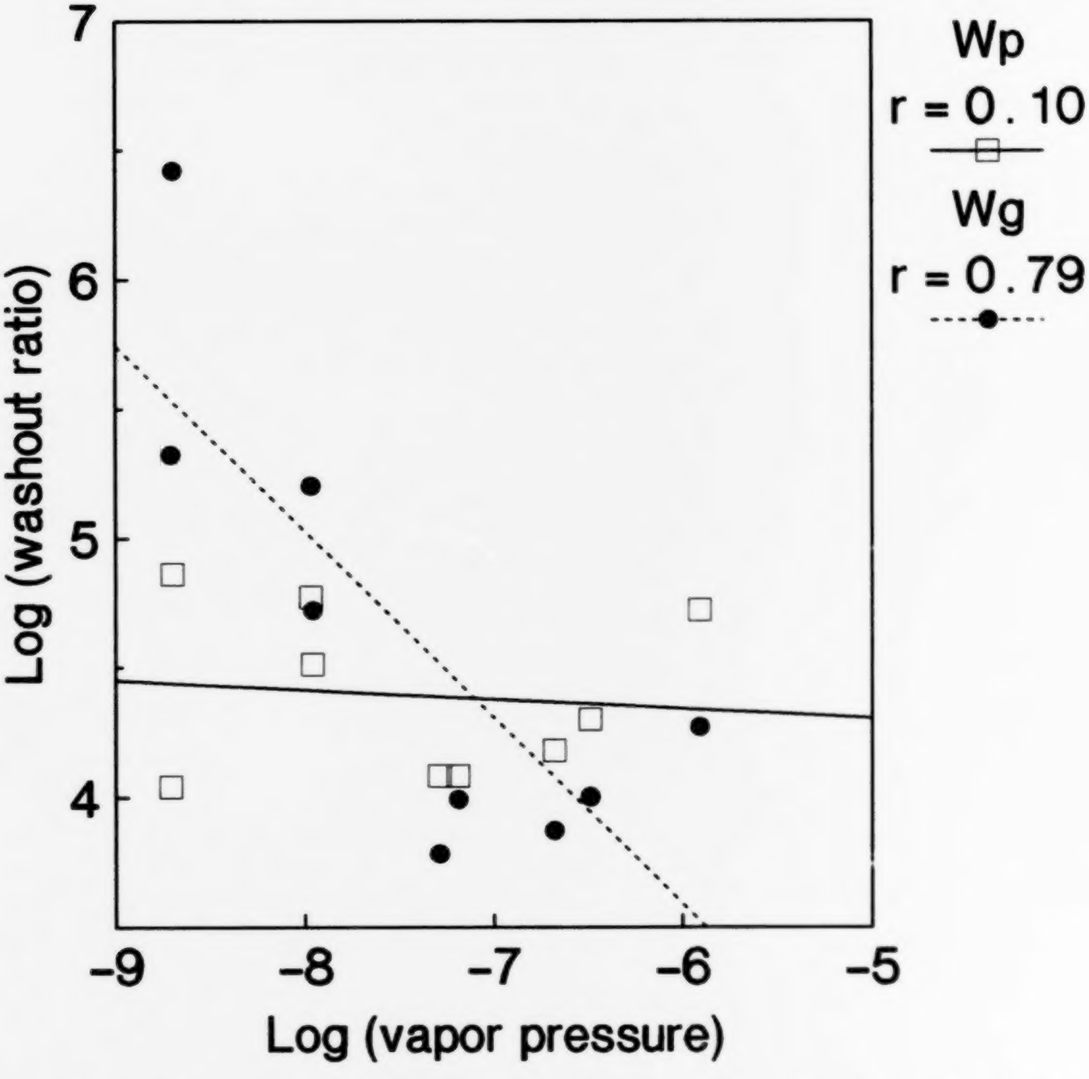

Figure 5-1. Washout ratios for each homologue (except the tetra dioxin homologue) as a function of the homologue's average vapor pressure.

From these measured washout variables we draw several conclusions: (a) particle scavenging is generally a somewhat more important process than gas scavenging; (b) total scavenging efficiency generally increases with level of chlorination; and (c) Henry's law constants for the less chlorinated homologues are in a range where there might be some PCDD/F volatilization from water in lakes (Thomas, 1982). These observations all suggest that the higher chlorinated homologues have a greater tendency to reach the sedimentary sinks than the less chlorinated homologues. In other words, wet depositional processes favor a sedimentary homologue profile which shows higher concentrations of the more chlorinated homologues. This is, in fact, what is seen.

GEOGRAPHIC VARIABILITY OF PCDD/F IN AIR

Analysis of air samples from locations other than Bloomington allows us to assess geographic variability and its causes. Figure 5-2 shows the average homologue profiles for air samples at our three sampled locations. Even though the Indianapolis and Trout Lake locations were only sampled for 2-week periods, it is clear that there are some significant differences between the locations.

Concentration Differences

The primary difference is in the concentrations. Average homologue totals from Indianapolis are 1.6 to 6 times higher than the corresponding homologue in Bloomington and 7 to 30 times higher than Trout Lake. However, when differences in the total suspended particle concentration at the three sites are taken into account, the factors are much smaller. Thus, the ratio of the total PCDD/F concentration to the total suspended particle concentration is only 2.5 times greater in Indianapolis than Trout Lake. That urban sites such as Indianapolis have more PCDD/F in their air is not surprising; there are clearly more numerous and more intense sources of these compounds in urban locations than in rural locations.

This concentration trend can also be found in the limited PCDD/F ambient air concentration data in the literature (Oehme *et al.*, 1986; Buck and Kirschmer, 1986; Nakano *et al.*, 1987; Rappe *et al.*, 1988; Smith *et al.*, 1988). These data are compiled in Table 5-4. Note, that the concentrations of our three sampling locations fall correctly on the continuum created moving from industrial to urban to suburban to rural. This assures us that our samples are representative of what is seen in ambient air.

Homologue Profile Comparisons

Other differences shown in Figure 5-2 are related to changes in the relative amounts of the various homologues for the three locations. The limited sampling time for the Indianapolis and Trout Lake locations means that these locations did not have the broad range of sample temperatures seen in Bloomington. Because temperature is a primary determinant of a homologue's vapor-to-particle ratio (see Chapter 4), it would not be prudent to use vapor and particle-bound concentrations separately in this discussion. Thus, we will only consider the total (vapor-plus-particle) PCDD/F concentrations and homologue patterns. The profiles show similarities: the tetrachlorodioxin and octachlorofuran levels are always low, and

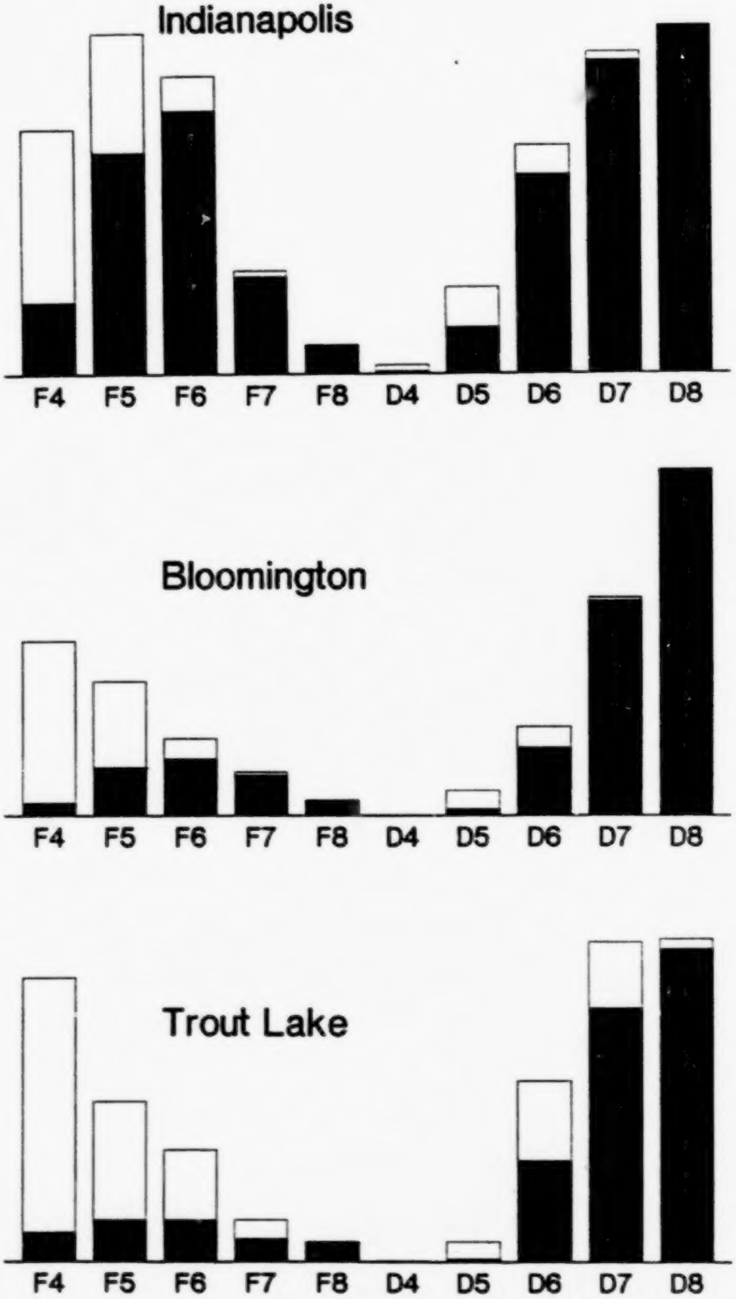

Figure 5-2. Average concentrations of the PCDD/F homologues (F4 to F8 and D4 to D8, respectively) in ambient air from Indianapolis, Indiana; Bloomington, Indiana; and Trout Lake, Wisconsin. The solid portion of the bar is particle-bound, while the blank portion is vapor phase. The total (vapor plus particle-bound) D8 concentrations are: Indianapolis, 920 fg/m^3; Bloomington, 590 fg/m^3; and Trout Lake, 90 fg/m^3. These values can be used as scale factor for each plot.

Table 5-4. Comparison of this study's air concentration measurements with those of previous workers. Samples in boldface are from this study.

Sample	Location Type	Total PCDF (pg/m^3)	Total PCDD (pg/m^3)
a	industrial	15	13
b	auto-tunnel	13	16
c	industrial	10	9
d	urban	8.8	8.6
e	urban & industrial	5.5	3.2
f	**Indianapolis**	**2.6**	**2.5**
g	suburban	0.74	1.8
h	**Bloomington**	**0.63**	**1.2**
i	suburban	0.50	1.0
j	**Trout Lake**	**0.18**	**0.24**

[a] Average of sites 6 and 7 from Tables 2-7 in Rappe _et_ _al_. (1988).

[b] Average of site 8 from Tables 2-7 in Rappe _et_ _al_. (1988).

[c] Average of CAM site from Table 2 in Smith _et_ _al_. (1988).

[d] Determined from Figure 4 in Nakano _et_ _al_. (1987).

[e] From Table 9 in Buck and Kirschmer (1986).

[g] Average of sites 1 and 2 from Tables 2-7 in Rappe _et_ _al_. (1988).

[i] Average of HRB site from Table 2 in Smith _et_ _al_. (1988).

the hepta- and octachlorodioxin levels are always high. There are also differences: The Trout Lake and Bloomington locations appear to be more similar to each other than to Indianapolis.

To compare the homologue profiles from the three locations in a more formal way, we performed a principal components analysis on the data from each individual sample. Homologue totals were normalized to the total PCDD and PCDF concentration. The first two components accounted for 56% of the variability between the samples and are plotted in Figure 5-3. Note that, although there is some overlap between individual Bloomington and Indianapolis samples, the four Indianapolis samples all have principal component 1 values greater than 1.5 and are on the edge of the Bloomington values. The three Trout Lake samples, however, all lie within the region where the majority of the Bloomington samples are seen; thus, they have essentially the same homologue profile as Bloomington. Clearly, there is a difference in the homologue profile between urban and suburban locations; suburban and rural locations seem to be more similar.

Summary

The observed geographic variability suggests the following atmospheric transport scenario. Urban air is contaminated with PCDD/F by proximity to the combustion sources of these compounds. As the air mass moves away from the urban area, it is diluted with cleaner air, lowering the PCDD and PCDF concentrations. As the air is transported, transformations occur, changing the homologue profile. One transformation is photodegradation of vapor-phase PCDD/F (Orth, 1988). The less chlorinated homologues have greater proportions of their total concentration in the vapor phase. Thus, vapor-phase photodegradation during the transport process would have a greater effect on the less chlorinated congeners. Like the washout process, these degradation processes would favor an ultimate homologue profile with enhanced concentrations of the more chlorinated homologues.

DEPOSITION OF PCDD AND PCDF

It is useful to compare the observed air and rain concentration data with flux data from sediments. This can be done qualitatively by comparing the homologue profiles, as well as quantitatively by comparing depositional fluxes.

Qualitative Comparison

The qualitative comparison is shown in Figure 5-4, which plots the average homologue profiles of Bloomington air and rain and of average Great Lakes sediment as reported by Czuczwa (1984). Note that all three profiles show octachlorodioxin to be the most abundant homologue. There appears to be considerable similarity between the particle-bound portion of air, total rain, and sediment. Thus, it appears that particle and wet deposition are important processes, and they should be studied quantitatively.

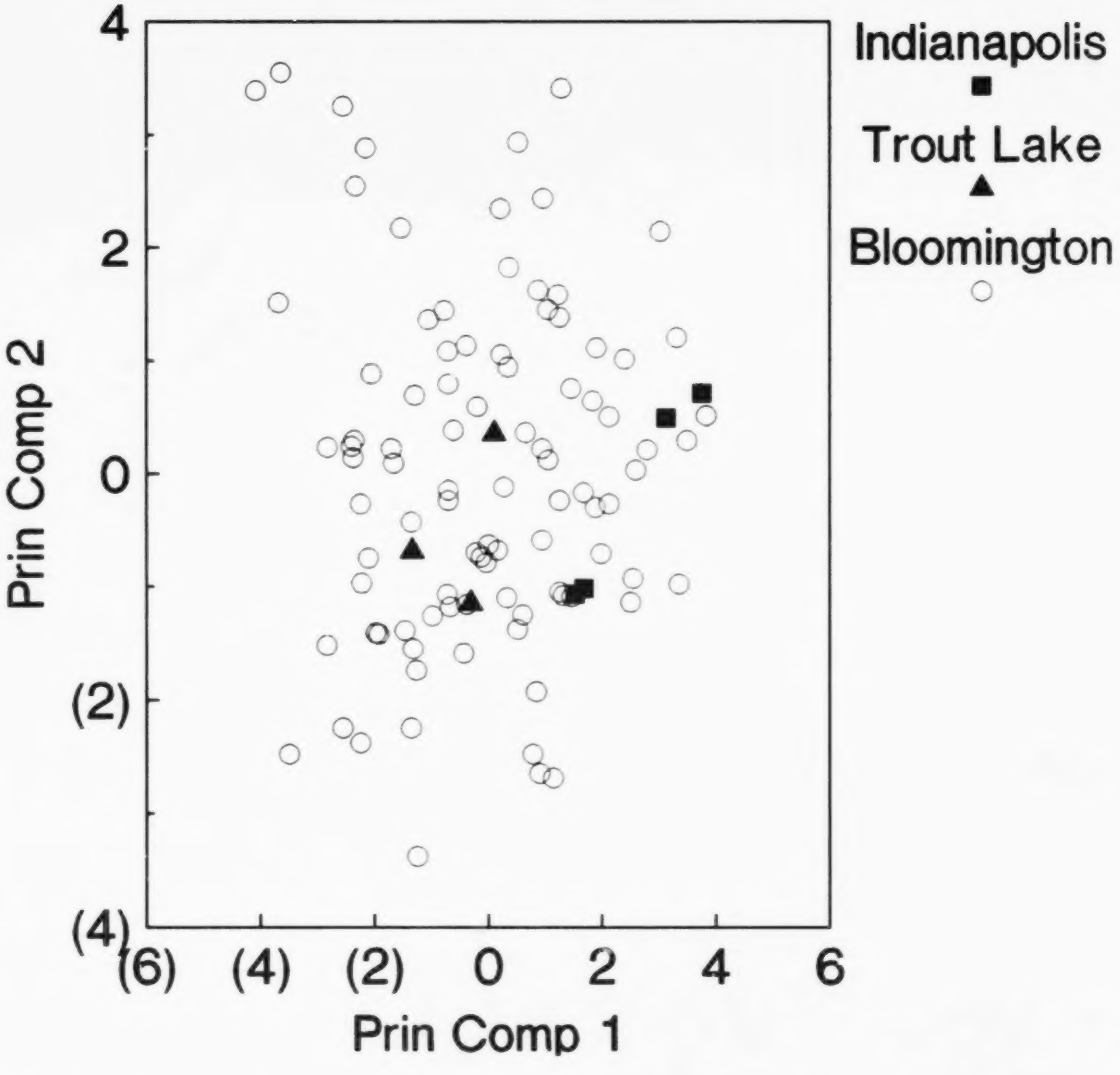

Figure 5-3. Principal components analysis of PCDD/F in all air samples; the first principal component *versus* the second principal components plotted. Numbers in parentheses are negative numbers.

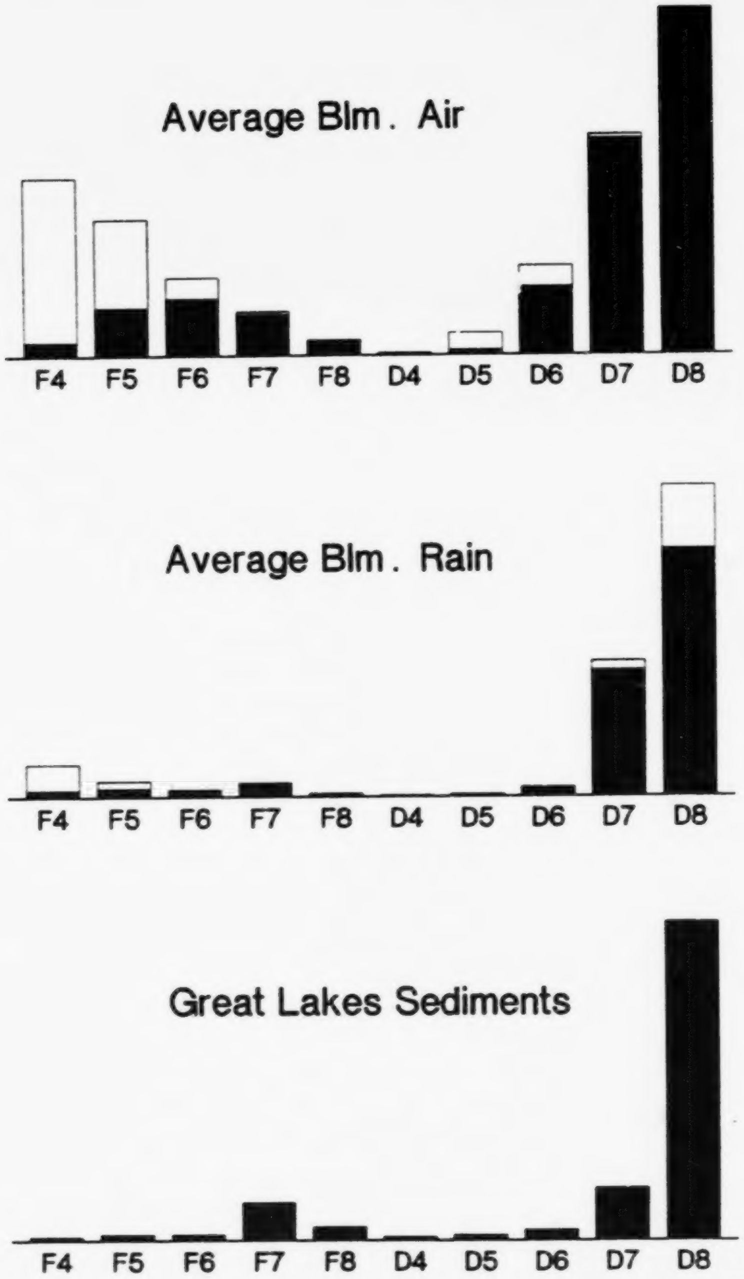

Figure 5-4. Average concentrations of PCDD/F homologues in air and rain taken in Bloomington, Indiana (this work), and in surface sediments from the Great Lakes (Czuczwa, 1984). The solid portion of the bar represents particle-bound for the air and rain samples, while the blank portion represents the vapor and dissolved phases, respectively. The total D8 concentrations are: Air, 590 fg/m^3; Rain, 54 pg/L; Great Lakes Sediment, 1100 pg/g. These values can be used as scale factor for each plot.

Quantitative Comparison

Deposition is best measured in terms of flux, which is the amount deposited per unit area per unit time. For rain, the flux can be easily calculated by multiplying the average rain concentration by the yearly rainfall (100 cm/yr in the Great Lakes region, as an estimate). For sediments, flux is calculated by determining the sediment deposition rate and the compound's concentration and by accounting for sediment focusing (not all sediment comes from the area directly above it).

Particle deposition from the atmosphere is dependent on the deposition velocity of the particle (V_d), which varies with the nature and size of the particle (Slinn *et al.*, 1978). There have been a number of differing measurements or estimates of the deposition velocity of atmospheric particles; these differences can be attributed to the species examined or the experimental method used. For example, McVeety and Hites (1988) reported a V_d of 1 cm/s for PAH, while from the same set of samples Swackhamer *et al.* (1988) reported a V_d of 0.2 cm/s for PCB. Both of these values lie within the range of V_d's reported in McMahon and Denison's (1979) review. Because we are interested in combustion-generated PCDD/F, we felt that the V_d estimated for PAH (a known product of combustion) would provide the best estimate of V_d. (PCBs, though similar in nature to PCDD/F, are not the result of combustion processes.) Vapor-phase deposition will depend on the rate of mass transfer between two phases, and it is highly dependent on the nature of the surface. Thus, vapor deposition to the surfaces of a smooth lake, a choppy lake, and a leaf are different. We have assumed that this is not an important process, and we have not made estimates of the associated flux. This assumption will be substantiated later.

Depositional flux estimates for Bloomington rain, air particles from all three locations, and average Great Lakes and Siskiwit Lake sediments are presented in Table 5-5. Given the errors in the analysis of each compartment, the inherent approximations necessary to make the calculations, and the difference in geographic locations, the air and rain fluxes are quite similar to those actually measured in sediment. For example, Siskiwit Lake, a remote lake on Isle Royal approximately 55 km south of Thunder Bay, Ontario, shows fluxes similar to those calculated at Trout Lake, the rural location. The Great Lakes average fluxes are similar to the total Bloomington values and to the Indianapolis particle values. This seems correct: There are both highly industrial and rural areas in the Great Lakes' airshed.

The greatest discrepancy appears to be in the octachlorodioxin flux, which is three to five times higher in the Great Lakes sediment than the fluxes from the atmospheric data. This could have several possible causes: (**a**) the inherent errors associated with these analyses, (**b**) additional sources of octachlorodioxin to the sediment, or (**c**) other depositional processes that we do not fully understand.

We can also use the Bloomington fluxes to estimate the relative importance of the wet and dry pathways. The geometric average dry-to-wet deposition ratio for the homologues was 6:1; the total (essentially a weighted average of the homologues) dry-to-wet ratio was 5:1. These data compare quite favorably with the 9:1 ratio reported by McVeety and Hites (1988) for PAH and with the 10:1 ratio reported for chloro-organics by Villeneuve and Cattini (1986), but are the reverse of the 1:3 ratio reported by Swackhamer *et al.* (1988) for PCBs. Clearly, the chosen

Table 5-5. Comparison of measured sediment and calculated atmospheric depositional fluxes at various locations.[a]

Location	Type	F4	F5	F6	F7	F8	D4	D5	D6	D7	D8	Total
Trout Lake	air part.	0.27	0.38	0.38	0.21	0.16	0.002	0.03	0.91	2.3	2.8	7.4
Bloomington	rain	0.57	0.28	0.13	0.24	0.07	0.03	0.04	0.16	2.3	5.4	9.2
Bloomington	air part.	0.69	2.3	2.6	2.0	0.82	0.01	0.41	3.7	11.7	19	43
Bloomington	dry + wet	1.3	2.6	2.7	2.2	0.89	0.04	0.46	3.9	14	24	52
Indianapolis	air part.	5.7	18	21	7.9	2.3	0.01	3.8	16	25	29	130
Avg. Great Lakes	sediment	1.2	1.9	1.8	11	4.0	1.2	1.7	3.1	15	94	140
Siskiwit Lake	sediment	0.47	0.16	0.06	0.63	0.13	0.83	0.38	0.32	2.2	18	23
Bloomington	dry/wet	1.2	8.2	20	8.3	12	0.33	10	23	5.1	3.4	4.7

[a] Sediment fluxes were calculated by Czuczwa (1984). All fluxes are expressed in $pg \cdot cm^{-2} yr^{-1}$.

V_d estimate impacts this number. Given our estimate, it is likely that dry deposition of particles is the more important of the two depositional pathways.

SOURCE-TO-SINK TRANSFORMATION EXPLANATION

We compared homologue profiles from the different compartments encountered between the sources and sinks of PCDD and PCDF. Because the concentration data from each compartment are reported in different units, we normalized the data to the total PCDD and PCDF concentration of each compartment. The normalized data were analyzed with a principal components procedure.

The first two principal components, which represent 57% of the variability, are plotted in Figure 5-5, which shows how the homologue profiles change between the sources and the sinks. The various combustion sources are spread around the plot and generally have a principal component 1 value greater than -1. This scatter indicates that these sources generate a broad spectrum of homologue profiles. The urban/industrial ambient air samples group together in the middle of the sources. Thus, the mixture of different emissions in an urban area produces a consistent profile. The suburban/rural air samples form a second subgroup, which has undergone some changes in profile so that their profiles are between the urban samples and the cluster of sediment samples.

Of particular interest are the samples connected by lines. These are the averages for the sample locations of this study. Note that when an air sample is split into its vapor and particle-bound constituents, the particle-bound portion is translated towards the sediment cluster while the vapor phase is moved away from the cluster. Similarly when the rain sample is split into the dissolved and particle-bound constituents, the particle-bound remains in the sediment cluster while the dissolved moves away from the cluster. Note also, that the vapor-particle-bound translation in air generally parallels the dissolved-particle-bound translation in rainwater. These translations indicate that particle deposition processes (wet and dry) control PCDD/F deposition because they are closer to the deposited (sediment) profile. This agrees with our data in Table 5-3 showing that particle washout is more important than vapor washout and justifies our neglect of dry vapor deposition.

SUMMARY

To summarize, the data support the following scenario. A broad range of PCDD and PCDF are injected into the atmosphere by numerous combustion sources, forming a uniform, urban, ambient air mixture. As the air mass moves away from the sources, it is diluted with cleaner air and starts to "age". Less chlorinated congeners are found to a greater extent in the vapor phase, and thus, they undergo a greater degree of photodegradation. This enhances the relative concentrations of the more chlorinated congeners. The particles with their enhanced load of the more chlorinated congeners are deposited by both wet and dry processes. Although the dry process dominates, the efficiency of the wet method improves for the more chlorinated congeners. Once in the water column, Henry's law constants predict greater vaporization to be occurring for the less chlorinated congeners.

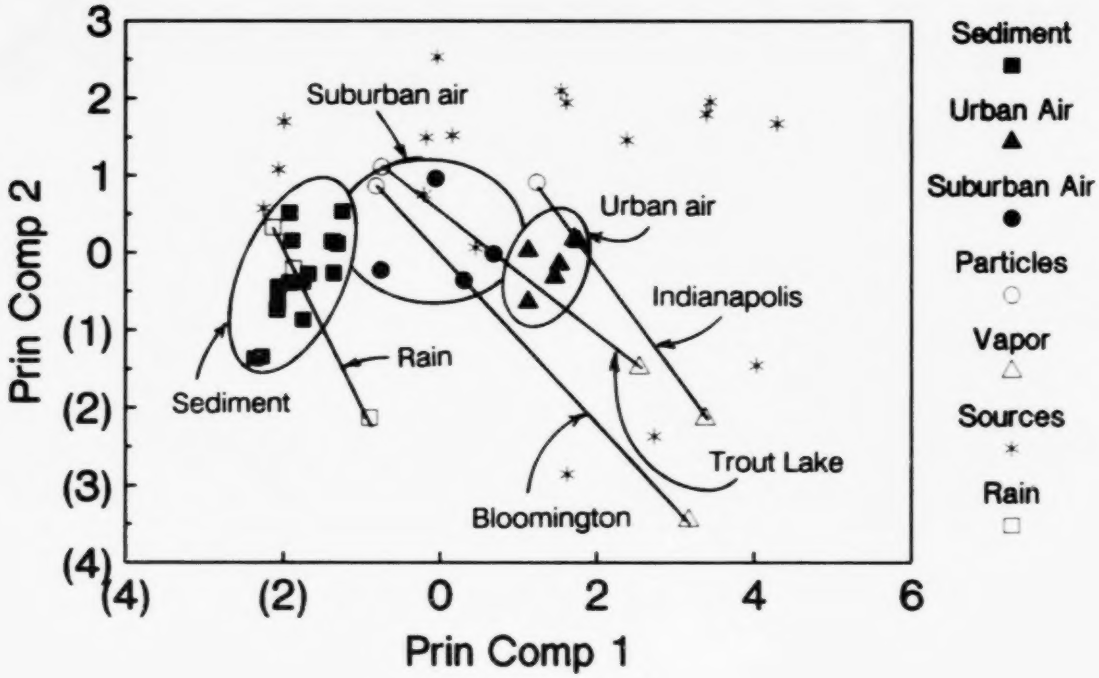

Figure 5-5. Principal components analysis of PCDD/F in various environmental samples reported in this work and the literature; the first principal component *versus* the second principal component is plotted. Multiple samples from any location were averaged to generate a single data set for each location. The data sources are: surface sediment data, from Czuczwa (1984); urban or industrial ambient air (vapor plus particle), from this study, Buck and Kirschmer (1986), Nakano *et al.* (1987), Rappe *et al.* (1988), and Smith *et al.* (1988); ambient air particles, this study; ambient air vapors, this study; combustion sources, Buser and Bosshardt (1978), Lustenhouwer *et al.* (1980), Liberti and Brocco (1982), Liberti *et al.* (1982), Olie *et al.* (1982), Rappe *et al.* (1983), Czuczwa and Hites (1986), Yasuhara *et al.* (1987), and Clement *et al.* (1988); rain, this study. Numbers in parentheses are negative numbers.

This further enhances the relative proportion of the more chlorinated congeners, which pass through the water column to the sediment.

Every process which occurs favors a homologue profile enriched in the more chlorinated congeners. It is, therefore, not surprising that the sediment profiles are most enriched in octachlorodioxin and that the next most abundant homologues are the heptachloro- dioxins and furans. Although the sedimentary octachlorofuran concentration is somewhat less than might be expected, in most of the combustion sources, it is one of the least abundant homologues. Therefore, its sediment levels may still represent an enhancement over its original abundance. Our data indicate that only the most chlorinated PCDD/F congeners are environmentally persistent. This finding may be of interest to policymakers because these congeners tend to be the least toxic.

CHAPTER 6

SUMMARY AND RECOMMENDATIONS

SUMMARY

This project has focused on the determination of PCDD and PCDF in ambient air and rain samples and on the comparison of the data from these environmental compartments with data from other environmental compartments. Its goal was to improve our understanding of the underlying parameters and characteristics that control the behavior of PCDD and PCDF as they are transported through the atmosphere from source to sink. It is useful to review the knowledge gained through this study and to discuss how it has extended our understanding of the behavior of PCDD/F in the environment.

This report supports the contention that the activity of man has caused the dramatic increase of PCDD/F concentrations in sediment deposited after 1940. This support comes from the comparison of the levels in urban, suburban, and rural areas. Certainly man makes his greatest impact on the environment in urban areas where there are numerous potential combustion sources. A continuum of ambient concentrations, with the highest concentrations seen in urban areas and the lowest concentrations seen in rural areas, was observed. Thus, ambient air PCDD/F levels mimic the amount of man's activity in the area, indicating that these compounds are primarily produced through anthropogenic sources.

Furthermore, ambient air and rain concentrations correspond to the sediment concentrations in terms of flux. This lends support to the idea that background environmental levels of PCDD/F are caused by PCDD/F entering the environment through the atmospheric pathway. This pathway is entered directly by combustion sources but only indirectly (if at all) by other sources. Thus, this project provides further support for the idea that combustion sources are the primary background environmental source of PCDD/F.

In the past, there has been difficulty in linking the combustion sources of these compounds to their sedimentary sinks because of differences in the homologue profiles of sources and sinks. This report has made that linkage in a much more conclusive manner. The linkage comes from the analysis of the characteristics and parameters of PCDD/F which control what occurs during transport and deposition.

This project showed that during transport there is partitioning between the vapor and particle-bound phases. This partitioning is controlled by the vapor pressure of the congener and the ambient temperature; the partitioning process favors a particle-bound concentration enriched in the more chlorinated congeners. The enriched particles were shown to deposit better than the vapor phase. Finally, estimates of Henry's law constants indicated that the more chlorinated congeners stand a better chance of being transported through the water column to sediment. Thus, every process which occurs favors a sediment profile enriched in the more chlorinated homologues, which is, in fact, what is seen. Therefore, the source and sink profiles are linked by the processes occurring during transport and deposition.

This project has clearly met its objectives. Two fundamental parameters of the individual congeners and one environmental characteristic have been shown to control the behavior of PCDD/F as they are transported from source to sink. The fundamental parameters are vapor pressure and Henry's law constant (both of which are estimated in this report). The primary environmental characteristic is ambient temperature. It is quite likely that other parameters (such as K_{OW}) and processes (such as photodegradation) also are important; these processes and parameters could affect the different congeners to differing degrees, but the extent of the effects could not be determined by the research reported here.

RECOMMENDATIONS FOR FUTURE WORK

Although this project has obviously improved our understanding of the environmental behavior of PCDD/F, there still remains work to be done. Some of the more important areas still needing research are noted below.

Air

A long-term study of a single site has been completed. Although alternate sites were compared, these were only analyzed for 2-week periods. Clearly, it is possible that Bloomington, Indiana, is not a typical suburban site. Thus, long-term studies of alternate locations might show temporal (or other) trends that were not seen in the Bloomington data. As a first choice, a more urban location (with its likely closeness to more and larger sources) would seem to be the best choice.

The ambient air analysis of PCDD/F needs to be supplemented by a particle size characterization. Particles of different sizes deposit from the atmosphere at different rates; thus, if PCDD/F are more prevalent on a particular particle size, then they could have a deposition velocity greater or less than the 1 cm/s estimate used for the flux calculations. This type of analysis would be best performed in an urban/industrial setting for two reasons. First, this could help characterize the types of particles on which PCDD/F are found in the sources. Second, a particle size fractionation would require splitting a single air particle sample into five to six different portions. This would substantially reduce the concentration factor; thus, higher concentration air samples would be necessary.

A final area which must be considered is the determination of rates of photodegradation. Although Orth (1988) has shown some indications of vapor-phase photodegradation for a few PCDD congeners, much work in this area remains to be completed. There are also questions about the possibility of photocatalytic formation of PCDD/F on particles (Koester, 1988). Clearly, it is necessary to understand these photodegradation or photoformation processes if we are to fully understand the environmental behavior of PCDD/F.

Rain

The concentrations measured in the rain samples reported here were close to detection limits. This limited the rain analysis to homologue data. We now know that urban areas have significantly higher ambient air concentrations than suburban areas; thus, if the rain sampler were operated in highly urban areas, it is likely that the concentrations would be raised sufficiently to allow congener-specific analysis in the rain samples. Furthermore, this could allow field estimates of the Henry's law constants for the individual congeners.

A second area of study which could supplement the rain data would be laboratory measurements of the Henry's law constants of the PCDD/F. This would allow us to assess if equilibrium is being achieved between the vapor and dissolved phases. These measurements could be done at specific temperatures so that the temperature-dependence of PCDD/F Henry's law constants could be determined.

Other Processes

The environmental behavior of PCDD/F is not controlled by air and rain processes alone. There are questions about the fate of these compounds once they reach the water column of a lake. How are they transported through the water column? Do they resuspend from the sediment and volatilize from the lake? To what extent are they bioconcentrated? Other questions relate to the pathway by which humans are exposed. Is it through the food chain, or is it respiration related? For example, given the ambient air concentration levels, it might be more important to study an indirect human pathway (such as deposition to grass, uptake by cows, and depuration to milk) rather than the direct inhalation pathway. Although there has been much preliminary research in these areas, there remains more work to be done; data from this report could be used in setting priorities.

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APPENDIX. DATABASE FOR PCDD/F IN AIR BY GC/MS PEAK

For each sample, the sample number, sample site, sample dates, average temperature in °F, total suspended particulate concentration in µg/m^3, and GC/MS peak data in fg/m^3 are presented. The first letter of the peak identifier signifies vapor (V) or particle-bound phase (P); the next letter indicates dioxin (D) or furan (F); the first number indicates the number of chlorines; and the second number indicates the peaks elution number within that homologue. For example, GC/MS peak VF4-10 indicates the vapor-phase concentration of the tenth tetrachlorofuran peak. The data were calculated on a spread sheet, and only the first two figures are significant. Key: nd- not detected, *- not measured.

SAMPLE	SITE	DATES	AVG T	TSP	VF4-1	VF4-2
1	IND	OCT. 27-30, 1987	53	59.8	7.6	17.0
2	IND	OCT. 30-2, 1987	71	85.5	14.6	29.3
3	IND	NOV. 2-4, 1987	73	121.9	17.4	31.3
4	IND	NOV. 4-6, 1987	58	74.3	8.7	16.3
5	TL	AUG. 10-13, 1987	80	23.1	1.7	4.6
6	TL	AUG. 13-19, 1987	83	21.0	3.9	6.5
7	TL	AUG. 16-19, 1987	76	10.9	10.0	3.0
8	SS	JULY 22-25, 1987	83	50.7	17.7	13.6
9	BMS	JULY 22-25, 1988	83	47.7	15.8	12.7
10	MCC	JULY 22-25, 1988	84	55.7	16.8	30.2
11	SS	JUNE 17-20, 1988	74	56.9	54.5	34.1
12	BMS	JUNE 17-20, 1988	89	68.1	28.4	35.5
13	MCC	JUNE 17-20, 1988	33	74.2	86.2	57.4
14	MCC	JUNE 17-20, 1988	83	72.4	59.5	39.7
15	SS	MAY 16-19, 1988	63	98.9	15.8	12.3
16	BMS	MAY 16-19, 1988	63	69.1	6.2	18.7
17	MCC	MAY 16-19, 1988	72	77.1	8.1	16.3
18	MCC	MAY 16-19, 1988	72	79.2	7.1	12.9
19	MCC	APR. 11-13, 1988	69	47.9	5.6	7.4
20	BMS	APR. 11-13, 1988	62	42.6	6.4	10.3
21	SS	APR. 11-13, 1988	62	39.1	4.2	8.4
22	BMS	MAR. 21-24, 1988	63	43.2	12.1	12.1
23	SS	MAR. 21-24, 1988	64	47.3	31.9	23.9
24	SS	MAR. 21-24, 1988	64	46.0	31.6	36.9
25	MCC	MAR. 21-24, 1988	55	72.8	29.9	29.9
26	SS	FEB. 26-29, 1988	44	48.5	14.0	9.3
27	BMS	FEB. 26-29, 1988	49	71.0	6.9	8.2
28	MCC	FEB. 26-29, 1988	47	60.6	9.4	10.8
29	MC	JAN. 18-21, 1988	44	31.7	10.6	11.9
30	BMS	JAN. 18-21, 1988	44	21.2	15.7	13.1
31	SS	JAN. 18-21, 1988	44	37.6	23.4	13.4
32	SS	JAN. 18-21, 1988	44	22.2	7.2	5.4
33	SS	DEC. 16-18, 1987	30	*	1.8	4.4
34	BMS	DEC. 16-18, 1987	30	39.8	4.2	6.9
35	MCC	DEC. 16-18, 1987	30	42.8	nd	5.0
36	SS	NOV. 20-23, 1987	42	38.3	3.6	4.3
37	BMS	NOV. 20-23, 1987	42	31.1	1.4	2.9
38	MCC	NOV. 20-23, 1987	42	57.7	2.3	6.3
39	MCC	OCT. 28-30, 1987	53	87.4	30.1	45.2
40	SS	OCT. 23-28, 1987	53	34.5	7.2	14.5
41	BMS	OCT. 23-26, 1987	54	32.8	1.1	13.7
42	MCC	SEP. 25-28, 1987	77	89.1	14.9	29.8
43	BMS	SEP. 25-28, 1987	76	99.7	21.2	42.5
44	SS	SEP. 25-28, 1987	78	52.1	6.0	12.0
45	SS	SEP. 25-28, 1987	78	49.3	11.3	22.7
46	MCC	AUG. 25-28, 1987	71	50.0	51.3	76.9
47	BMS	AUG. 25-28, 1987	73	29.9	8.4	2.5
48	BMS	JULY 27-30, 1987	86	37.9	40.8	30.6
49	SS	JULY 27-30, 1987	93	44.5	36.6	19.5
50	SS	JULY 27-30, 1987	93	44.7	31.5	13.5
51	MCC	JUNE 26-29, 1987	82	46.5	19.5	63.4
52	BMS	JUNE 26-29, 1987	79	37.9	13.9	17.3

SAMPLE	SITE	DATES	AVG T	TSP	VF4-1	VF4-2
53	SS	JUNE 26-29, 1987	73	48.1	22.0	27.5
54	SS	JUNE 26-29, 1987	83	48.9	15.4	15.4
55	MCC	MAY 15-18, 1987	81	69.4	68.6	45.7
56	SS	MAY 15-18, 1987	81	56.9	9.4	11.3
57	SS	MAY 15-18, 1987	81	67.2	7.5	10.0
58	MCC	APR. 24-27, 1987	67	61.4	5.5	5.5
59	SS	APR. 24-27, 1987	68	48.4	2.9	5.7
60	BMS	APR. 24-27, 1987	62	50.3	16.3	32.7
61	MCC	MAR. 27-30, 1987	57	53.1	14.8	20.7
62	BMS	MAR. 25-27, 1987	52	27.6	11.9	8.9
63	SS	MAR. 4-8, 1987	65	47.8	11.7	50.0
64	SS	MAR. 3-8, 1987	60	46.2	10.7	36.3
65	MCC	FEB. 25-27, 1987	48	98.5	55.7	204.3
66	BMS	FEB. 25-27, 1987	51	53.6	9.1	42.3
67	SS	FEB. 19-21, 1987	52	61.3	3.9	32.2
68	SS	FEB. 19-21, 1987	52	*	6.7	31.4
69	SS	FEB. 11-13, 1987	49	*	4.3	17.4
70	SS	FEB. 11-13, 1987	49	60.7	nd	16.0
71	BMS	JAN. 26-28, 1987	23	50.0	nd	17.7
72	SS	JAN. 21-23, 1987	29	29.4	nd	13.4
73	MCC	JAN. 7-9, 1987	39	*	1.1	3.0
74	BMS	DEC. 16-18, 1986	50	*	2.2	5.4
75	MCC	DEC. 2-5, 1986	37	*	3.4	6.0
76	MCC	OCT. 8-10, 1986	65	*	32.8	43.7
77	MCC	SEP. 24-26, 1986	85	*	53.7	107.4
78	SPEA	JUNE 16-19, 1986	75	*	21.1	36.1
79	SPEA	MAY 27-29, 1986	78	*	53.9	47.2
80	SPEA	MAY 12-14, 1986	71	*	108.7	87.0
81	SPEA	APR. 28-1, 1986	65	*	11.0	21.9
82	SPEA	APR. 15-17, 1986	55	*	5.2	17.2
83	SPEA	MAR. 27-30, 1986	61	*	21.4	21.4
84	SPEA	MAR. 13-16, 1986	54	*	15.9	13.9
85	SPEA	FEB. 25-28, 1986	35	*	10.8	43.1
86	SPEA	FEB. 6-8, 1986	35	*	10.3	41.3
87	SPEA	JAN. 27-30, 1986	22	*	27.3	72.7
88	SPEA	JAN. 7-9, 1986	26	*	6.0	33.0
89	SPEA	DEC. 19-22, 1985	22	*	10.5	42.2
90	SPEA	DEC. 8-10, 1985	48	*	12.2	18.4
91	SPEA	NOV. 25-27, 1985	53	*	9.2	18.3
92	SPEA	NOV. 14-17, 1985	53	*	10.6	15.9
93	SPEA	OCT. 28-31, 1985	59	*	7.2	14.5
94	SPEA	OCT. 14-16, 1985	71	*	13.4	10.0
95	SPEA	SEP. 24-27, 1985	63	*	11.4	15.7
96	SPEA	SEP. 19-21, 1985	80	*	15.9	23.8
97	SPEA	SEP. 9-12, 1985	77	*	8.3	17.4
98	SPEA	AUG. 30-2, 1985	83	*	33.6	50.4
99	SPEA	AUG. 23-25, 1985	82	*	5.5	19.4
100	SPEA	JUN. 11-13, 1985	68	*	14.8	21.1
101	SPEA	APR. 26-28, 1985	81	*	7.2	10.2
102	SPEA	MAR. 12-14, 1985	57	*	3.0	3.0

S-#	VF4-3	VF4-4	VF4-5	VF4-6	VF4-7	VF4-8	VF4-9	VF4-10
1	26.5	22.7	26.5	30.3	41.6	77.6	17.0	11.4
2	41.0	29.3	46.8	52.7	64.4	108.3	23.4	11.7
3	52.1	27.8	52.1	59.0	72.9	111.1	41.7	17.4
4	20.7	16.3	21.8	21.8	29.4	48.9	10.9	5.4
5	6.7	5.0	5.9	6.7	4.2	10.1	2.9	1.7
6	13.0	7.2	5.9	10.4	3.3	10.4	2.6	2.6
7	11.0	3.0	3.0	6.0	4.5	6.0	1.0	1.5
8	5.5	8.2	5.5	9.5	24.5	32.7	13.6	2.7
9	6.3	12.7	7.9	9.5	47.5	22.2	12.7	1.6
10	8.4	13.4	8.4	20.1	67.1	57.0	16.8	6.7
11	13.6	20.5	20.5	20.5	272.7	54.5	54.5	13.6
12	7.1	14.2	14.2	21.3	312.0	28.4	14.2	nd
13	28.7	43.1	28.7	28.7	660.6	57.4	14.4	14.4
14	9.9	19.8	19.8	29.8	456.3	39.7	9.9	9.9
15	7.0	10.5	nd	12.3	19.3	35.1	5.3	3.5
16	8.3	20.7	10.4	16.6	29.0	89.2	8.3	4.1
17	5.4	8.1	8.1	8.1	10.8	29.8	6.8	4.1
18	4.7	7.1	3.5	7.1	7.1	25.9	4.7	1.2
19	nd	nd	nd	8.3	6.5	16.7	5.6	0.9
20	2.6	7.7	5.1	15.4	15.4	38.5	9.0	2.6
21	9.8	2.8	2.8	12.6	19.5	44.6	5.6	1.4
22	25.1	10.0	19.1	20.1	28.1	40.2	8.0	5.0
23	87.6	47.8	67.7	87.6	95.6	151.3	27.9	19.9
24	121.2	84.3	94.9	84.3	147.6	216.1	42.2	26.4
25	67.2	41.1	63.5	52.3	82.1	164.3	18.7	14.9
26	12.8	9.3	11.7	14.0	26.9	28.0	12.8	3.5
27	16.5	12.3	15.1	15.1	24.7	38.4	13.7	4.1
28	21.6	17.5	16.2	14.8	37.8	58.0	8.1	5.4
29	23.8	15.8	18.5	18.5	35.6	52.8	7.9	4.0
30	22.3	15.7	20.9	24.9	31.4	44.5	15.7	7.9
31	16.7	10.0	10.0	23.4	36.8	46.9	21.8	11.7
32	6.6	5.4	6.0	8.4	13.1	23.9	5.4	2.4
33	7.5	3.5	5.7	5.3	7.5	14.6	2.2	0.9
34	5.3	4.8	6.4	5.3	7.4	11.6	3.2	0.5
35	5.0	2.5	3.7	4.5	6.6	9.1	3.3	2.1
36	12.3	6.5	8.7	7.2	13.0	26.7	5.0	3.6
37	10.0	5.7	6.9	3.7	3.7	11.4	2.3	1.1
38	12.5	7.8	9.4	7.8	15.6	29.7	3.9	1.6
39	67.8	52.7	60.2	180.7	105.4	301.2	37.7	15.1
40	49.3	29.0	34.8	29.0	26.1	40.6	17.4	8.7
41	28.4	18.2	20.5	19.3	23.9	36.4	10.2	11.4
42	34.8	19.9	29.8	149.2	149.2	59.7	nd	nd
43	28.3	14.2	56.7	311.6	56.7	70.8	nd	nd
44	23.9	17.9	17.9	113.6	17.9	35.9	9.0	nd
45	22.7	11.3	14.2	113.5	17.0	28.4	8.5	nd
46	51.3	38.5	64.1	538.6	51.3	64.1	25.6	nd
47	6.7	1.7	5.9	29.3	4.2	6.7	nd	nd
48	30.6	25.5	25.5	40.8	61.2	35.7	5.1	5.1
49	19.5	24.4	14.6	34.1	70.7	17.1	4.9	nd
50	18.0	18.0	13.5	33.7	53.9	18.0	4.5	nd
51	48.8	63.4	34.2	29.3	195.2	58.5	9.8	9.8
52	17.3	8.7	17.3	13.9	48.5	55.4	1.7	6.9

S-#	VF4-3	VF4-4	VF4-5	VF4-6	VF4-7	VF4-8	VF4-9	VF4-10
53	11.0	5.5	2.8	27.5	13.8	93.6	13.8	8.3
54	9.3	7.7	9.3	6.2	55.5	12.3	6.2	3.1
55	57.2	34.3	45.7	22.9	194.3	57.2	11.4	11.4
56	13.2	11.3	23.5	15.0	9.4	16.9	4.7	2.8
57	15.0	10.0	25.0	20.0	10.0	17.5	5.0	2.5
58	14.6	7.3	10.9	10.9	69.2	29.1	5.5	3.6
59	18.6	11.4	14.3	17.1	40.0	51.4	8.6	7.1
60	130.8	65.4	130.8	196.2	261.5	294.2	179.8	163.5
61	47.2	17.7	32.5	26.6	100.3	106.2	11.8	5.9
62	7.4	11.9	14.9	3.0	37.2	53.6	6.0	3.0
63	33.4	16.7	28.4	16.7	65.1	48.4	13.3	10.0
64	35.2	23.5	24.5	11.7	35.2	45.9	8.5	6.4
65	185.7	86.7	136.2	61.9	253.8	185.7	43.3	18.6
66	36.2	16.1	35.2	14.1	30.2	41.3	11.1	8.1
67	19.5	13.6	15.6	9.7	17.5	32.2	7.8	5.8
68	33.6	17.9	22.4	11.2	20.2	43.7	11.2	6.7
69	34.7	21.7	32.6	34.7	43.4	78.2	21.7	8.7
70	25.6	12.8	24.0	22.4	22.4	54.3	8.0	4.8
71	12.8	5.9	11.8	13.8	13.8	27.6	5.9	5.9
72	12.3	4.5	9.0	11.2	31.4	29.1	5.6	2.2
73	7.8	3.7	3.7	3.0	15.5	10.3	1.8	1.1
74	9.9	3.6	5.4	4.9	14.3	14.3	4.0	1.8
75	9.4	3.4	4.3	5.1	34.9	18.7	4.3	1.7
76	10.9	54.6	27.3	43.7	229.3	60.1	10.9	5.5
77	40.3	120.9	80.6	107.4	550.6	134.3	13.4	26.9
78	18.1	30.1	30.1	42.1	102.4	102.4	12.0	12.0
79	33.7	23.6	33.7	33.7	107.9	64.0	20.2	13.5
80	79.7	101.5	108.7	72.5	253.7	144.9	43.5	21.7
81	21.9	35.1	30.7	30.7	70.2	76.8	13.2	8.8
82	20.6	13.7	18.9	13.7	34.4	51.5	17.2	3.4
83	16.1	21.4	26.8	26.8	50.9	93.7	10.7	8.0
84	23.8	15.9	19.8	19.8	39.7	79.3	9.9	5.9
85	43.1	39.5	35.9	57.5	57.5	158.1	28.8	14.4
86	41.3	31.0	36.2	41.3	51.6	105.9	20.7	7.7
87	118.1	109.0	90.8	45.4	81.8	417.8	27.3	18.2
88	33.0	24.0	27.0	30.0	30.0	63.0	12.0	7.5
89	68.5	73.8	58.0	52.7	73.8	221.4	26.4	10.5
90	39.8	18.4	21.4	55.1	30.6	64.3	9.2	4.6
91	21.4	9.2	15.3	9.2	61.1	30.6	6.1	3.1
92	29.2	13.3	15.9	8.0	53.1	55.7	8.0	4.0
93	24.8	10.3	14.5	10.3	37.2	35.1	8.3	5.2
94	33.4	13.4	21.7	50.1	10.0	56.8	6.7	3.3
95	14.3	11.4	11.4	48.5	22.8	34.2	7.1	5.7
96	23.8	15.9	19.8	71.3	27.7	47.6	11.9	5.9
97	6.4	4.1	5.5	17.4	11.9	19.3	6.4	2.8
98	42.0	29.4	37.8	151.2	42.0	58.8	16.8	8.4
99	22.2	11.1	16.6	105.4	16.6	19.4	5.5	2.8
100	14.8	12.7	16.9	65.4	16.9	16.9	nd	nd
101	10.2	10.2	10.2	16.3	14.3	30.6	4.1	3.1
102	7.5	5.2	3.0	9.0	4.5	9.0	0.7	0.7

S-#	VF4-11	VF4-12	VF4-13	VD4	VF5-1	VF5-2	VF5-3	VF5-4
1	87.0	15.1	5.7	20.3	5.6	2.8	2.8	52.9
2	140.5	23.4	11.7	12.3	22.2	9.5	6.4	120.8
3	159.8	34.7	13.9	18.0	23.9	12.0	8.0	143.6
4	47.9	9.8	3.3	5.9	16.0	4.9	2.5	45.5
5	16.8	3.8	3.4	nd	1.6	1.0	0.7	9.8
6	14.3	3.9	5.2	nd	2.4	1.9	0.5	11.3
7	5.0	3.0	1.5	2.9	3.2	2.4	0.8	6.4
8	32.7	5.5	8.2	nd	7.7	2.3	1.5	7.7
9	25.3	6.3	9.5	nd	9.2	2.6	1.3	13.1
10	63.7	13.4	10.1	nd	12.6	5.0	nd	27.7
11	81.8	13.6	20.5	nd	22.3	22.3	2.8	36.2
12	49.6	14.2	7.1	nd	9.7	19.5	3.2	50.3
13	57.4	14.4	8.6	nd	16.2	28.3	6.1	101.2
14	39.7	9.9	nd	nd	9.9	19.8	5.0	89.2
15	36.8	7.0	5.3	nd	11.7	5.9	nd	nd
16	58.1	6.2	4.1	nd	nd	nd	nd	31.4
17	27.1	6.8	5.4	nd	nd	4.6	nd	13.8
18	21.2	2.4	2.4	nd	2.0	3.0	nd	14.2
19	27.8	0.9	3.7	nd	2.1	4.3	nd	5.3
20	39.8	3.9	1.3	nd	5.5	8.3	nd	19.3
21	39.1	2.8	5.6	nd	7.8	11.7	3.9	23.5
22	38.2	10.0	4.0	5.4	14.9	6.6	3.3	56.4
23	179.2	31.9	15.9	nd	74.1	21.2	21.2	195.9
24	221.4	42.2	21.1	89.2	33.8	16.9	22.6	203.0
25	119.5	18.7	11.2	12.2	70.4	16.6	16.6	157.4
26	39.7	10.5	2.3	nd	5.8	5.8	1.0	13.5
27	43.9	8.2	6.9	nd	2.7	3.6	0.9	15.4
28	40.5	6.7	4.0	nd	13.1	2.8	2.8	32.8
29	47.5	10.6	6.6	nd	6.1	8.1	2.0	30.3
30	34.0	14.4	6.5	nd	6.5	13.0	4.3	25.9
31	46.9	18.4	13.4	nd	8.1	nd	nd	18.9
32	23.9	6.0	3.6	9.8	nd	4.8	nd	12.0
33	8.8	1.8	nd	7.1	1.8	1.0	0.8	5.9
34	13.2	nd	nd	nd	2.7	2.3	nd	5.4
35	11.6	nd	nd	nd	nd	nd	1.3	4.0
36	24.5	5.8	2.9	nd	6.1	1.4	0.7	19.0
37	11.1	2.3	0.9	4.2	2.0	5.9	2.0	16.7
38	23.4	3.1	1.6	30.0	2.4	8.0	1.6	26.4
39	188.3	22.6	15.1	102.0	58.0	12.9	nd	109.5
40	46.4	8.7	1.4	nd	nd	11.3	3.8	54.6
41	31.9	11.4	4.6	nd	3.7	0.9	nd	27.9
42	64.7	9.9	9.9	53.2	21.1	47.6	10.6	200.9
43	70.8	14.2	7.1	10.4	14.9	36.2	4.3	51.1
44	26.9	6.0	12.0	4.9	3.7	9.3	0.9	32.4
45	28.4	5.7	11.3	nd	5.4	9.0	nd	30.6
46	76.9	25.6	25.6	63.8	26.0	17.3	5.8	52.0
47	10.9	1.7	5.0	nd	19.6	4.3	1.7	25.5
48	35.7	15.3	15.3	30.4	9.8	6.5	3.3	36.0
49	29.3	12.2	12.2	50.3	8.2	8.2	nd	24.5
50	22.5	9.0	9.0	36.7	11.6	9.9	3.3	33.1
51	58.5	9.8	4.9	nd	19.7	74.9	7.9	141.9
52	31.2	13.9	12.1	nd	20.3	45.7	10.2	76.1

S-#	VF4-11	VF4-12	VF4-13	VD4	VF5-1	VF5-2	VF5-3	VF5-4
53	16.5	13.8	11.0	nd	44.6	40.2	nd	53.5
54	15.4	6.2	3.1	nd	16.9	20.2	3.4	54.0
55	57.2	5.7	11.4	nd	12.2	36.6	6.1	109.9
56	24.5	7.5	8.5	nd	7.8	27.3	3.9	66.4
57	27.5	6.2	10.0	nd	5.1	20.5	1.7	58.1
58	32.8	5.5	3.6	nd	3.2	9.7	1.6	58.4
59	57.1	11.4	4.3	nd	22.3	6.7	4.5	80.1
60	751.9	261.5	65.4	1.4	nd	nd	nd	683.9
61	76.7	11.8	5.9	nd	31.8	19.1	9.6	114.6
62	23.8	8.9	4.5	nd	14.5	7.3	2.4	36.3
63	51.7	16.7	10.0	122.0	7.1	17.6	1.8	63.5
64	38.4	7.5	4.3	122.0	8.9	6.7	2.2	37.8
65	154.8	31.0	12.4	475.0	16.7	10.0	6.7	113.7
66	41.3	9.1	5.0	112.0	2.1	4.3	1.1	39.3
67	27.3	4.9	1.9	69.6	1.7	3.3	0.8	22.6
68	40.3	9.0	6.7	82.8	2.1	10.4	1.0	31.1
69	76.0	13.0	6.5	nd	nd	nd	3.5	56.2
70	73.5	9.6	4.8	52.3	nd	nd	2.5	41.7
71	13.8	3.9	2.0	27.1	nd	nd	0.4	5.1
72	26.9	2.2	1.1	21.2	nd	nd	0.5	14.1
73	6.7	1.5	1.5	12.2	0.4	0.8	0.3	4.9
74	13.4	3.6	1.8	nd	2.0	3.4	nd	11.2
75	11.9	4.3	1.7	nd	0.4	2.4	0.4	7.1
76	71.0	10.9	5.5	nd	nd	nd	25.1	141.2
77	134.3	26.9	13.4	nd	nd	30.3	48.5	273.1
78	120.4	30.1	18.1	nd	nd	nd	7.7	80.8
79	101.1	53.9	40.5	24.2	nd	nd	3.2	64.7
80	181.2	58.0	29.0	nd	nd	nd	5.5	116.5
81	87.8	26.3	6.6	4.5	nd	nd	8.0	59.7
82	65.3	13.7	5.2	9.0	nd	nd	6.7	72.2
83	107.1	26.8	16.1	12.2	nd	nd	3.7	81.5
84	75.3	17.8	9.9	11.5	nd	nd	6.1	65.4
85	82.7	14.4	2.2	24.0	nd	nd	4.1	41.5
86	67.1	10.3	5.2	50.7	nd	nd	5.2	51.7
87	72.7	9.1	nd	63.5	nd	nd	8.4	27.6
88	36.0	4.5	nd	15.9	nd	nd	1.3	10.5
89	63.2	nd	nd	22.0	nd	nd	4.9	15.5
90	38.3	6.1	1.5	16.3	1.5	0.8	4.6	32.3
91	27.5	6.1	3.1	20.0	1.8	5.5	7.4	40.6
92	39.8	8.0	2.7	12.6	2.6	0.9	6.0	40.4
93	35.1	8.3	4.1	10.1	0.6	0.6	5.5	27.0
94	36.8	6.7	1.7	12.1	nd	nd	7.6	60.5
95	31.4	5.7	4.3	74.4	4.4	16.2	1.0	12.2
96	43.6	9.9	5.9	97.4	nd	42.2	1.2	16.9
97	17.9	4.6	0.9	110.0	0.3	2.8	0.7	6.2
98	58.8	12.6	4.2	186.0	nd	nd	nd	43.9
99	27.7	11.1	5.5	182.0	5.8	56.2	1.4	17.3
100	21.1	2.1	8.4	35.7	11.9	nd	3.0	35.7
101	20.4	4.1	1.0	16.1	3.4	0.9	1.7	30.1
102	4.5	1.5	0.7	10.2	2.2	1.1	2.2	10.8

S-#	VF5-5	VF5-6	VF5-7	VF5-8	VF5-9	VF5-10	VF5-11	VF5-12
1	13.9	36.2	13.9	13.9	11.1	16.7	11.1	9.7
2	31.8	76.3	31.8	31.8	22.2	38.1	35.0	38.1
3	31.9	71.8	39.9	55.9	31.9	47.9	63.8	47.9
4	9.8	25.8	12.3	11.1	8.6	12.3	11.1	12.3
5	2.0	5.9	1.6	2.6	1.3	2.6	2.6	2.9
6	2.4	4.7	1.9	2.4	1.9	2.8	2.8	3.3
7	2.4	2.8	1.2	2.4	1.2	1.6	1.6	2.0
8	3.1	17.8	4.6	10.0	3.9	6.2	6.2	11.6
9	3.3	11.8	3.3	10.5	2.6	5.2	5.9	8.5
10	7.5	45.3	10.1	25.1	10.1	17.6	20.1	30.2
11	8.4	33.4	11.1	27.8	5.6	22.3	22.3	27.8
12	9.7	32.4	11.4	29.2	9.7	16.2	19.5	25.9
13	24.3	66.8	16.2	44.5	12.1	32.4	24.3	40.5
14	19.8	49.5	12.4	29.7	9.9	22.3	19.8	29.7
15	nd	27.8	8.8	11.7	8.8	16.1	17.6	24.9
16	15.7	66.6	19.6	17.6	13.7	19.6	17.6	35.3
17	4.6	15.0	5.8	9.2	4.6	9.2	11.5	9.2
18	4.1	24.4	6.1	10.2	4.1	10.2	10.2	8.1
19	3.2	20.2	6.4	12.8	5.3	8.5	12.8	14.9
20	8.3	33.0	9.6	11.0	9.6	11.0	9.6	11.0
21	15.6	50.8	13.7	13.7	11.7	13.7	13.7	27.4
22	13.3	29.9	10.0	13.3	13.3	14.9	16.6	18.2
23	42.4	95.3	37.1	37.1	31.8	52.9	47.6	58.2
24	62.0	140.9	56.4	56.4	50.7	62.0	56.4	67.7
25	33.1	82.8	29.0	24.9	24.9	33.1	24.9	33.1
26	3.9	8.7	4.8	7.7	2.9	2.9	7.7	7.7
27	5.4	12.7	4.5	9.1	3.6	8.2	7.3	3.6
28	7.5	20.6	8.4	8.4	4.7	7.5	5.6	5.6
29	6.1	16.2	6.1	6.1	6.1	6.1	4.0	6.1
30	8.6	17.3	8.6	8.6	8.6	8.6	10.8	8.6
31	5.4	16.2	5.4	5.4	2.7	5.4	2.7	8.1
32	3.6	8.4	3.6	3.6	3.6	4.8	4.8	4.8
33	1.0	3.4	1.6	1.8	1.6	2.1	2.3	2.1
34	1.5	3.5	2.3	4.2	1.5	2.3	3.1	1.9
35	1.3	3.3	2.2	3.5	1.3	1.8	3.1	1.6
36	4.7	13.6	4.7	6.8	4.1	4.7	4.1	4.7
37	3.9	9.8	3.4	2.9	2.4	2.9	2.4	2.0
38	6.4	15.2	6.4	6.4	4.0	4.8	3.2	3.2
39	25.8	77.3	32.2	48.3	19.3	32.2	25.8	22.5
40	15.1	33.9	11.3	15.1	11.3	13.2	13.2	11.3
41	7.4	20.4	7.4	7.4	6.5	7.4	7.4	7.4
42	42.3	105.7	31.7	31.7	21.1	31.7	31.7	47.6
43	17.0	46.8	12.8	12.8	6.4	12.8	10.6	23.4
44	5.6	14.8	5.6	6.5	3.7	5.6	4.6	7.4
45	6.3	16.2	5.4	7.2	3.6	6.3	11.7	13.5
46	10.1	28.9	15.9	15.9	4.3	7.2	5.8	8.7
47	6.8	14.5	6.8	6.8	4.3	5.1	5.1	8.5
48	6.5	22.9	6.5	9.8	6.5	9.8	8.2	11.4
49	8.2	12.2	4.1	12.2	4.1	6.1	6.1	6.1
50	8.3	16.6	6.6	13.2	6.6	9.9	9.9	11.6
51	43.4	102.5	31.5	31.5	23.7	39.4	39.4	47.3
52	22.8	45.7	15.2	17.8	17.8	22.8	20.3	17.8

S-#	VF5-5	VF5-6	VF5-7	VF5-8	VF5-9	VF5-10	VF5-11	VF5-12
53	22.3	26.8	4.5	13.4	nd	11.2	2.2	13.4
54	13.5	30.4	11.8	15.2	8.4	13.5	16.9	20.2
55	33.6	79.3	30.5	18.3	12.2	30.5	15.3	27.5
56	19.5	39.0	15.6	19.5	13.7	23.4	23.4	23.4
57	15.4	35.9	12.0	12.0	6.8	13.7	13.7	15.4
58	13.0	42.2	14.6	14.6	8.1	14.6	9.7	13.0
59	22.3	66.8	20.0	20.0	17.8	26.7	22.3	31.2
60	52.6	131.5	52.6	78.9	52.6	52.6	52.6	52.6
61	38.2	98.7	28.7	25.5	19.1	31.8	19.1	25.5
62	10.9	24.2	7.3	7.3	4.8	8.5	6.1	7.3
63	14.1	37.0	10.6	15.9	10.6	14.1	14.1	17.6
64	8.9	23.4	6.7	6.7	4.5	7.8	5.6	7.8
65	23.4	60.2	20.1	20.1	20.1	23.4	10.0	13.4
66	11.7	25.5	7.4	8.5	7.4	9.6	7.4	8.5
67	6.7	15.1	5.0	6.7	5.0	6.7	4.2	5.0
68	8.3	20.7	5.2	9.3	6.2	7.3	5.2	6.2
69	19.3	28.1	10.5	10.5	7.0	10.5	7.0	10.5
70	15.9	24.5	8.6	8.6	7.4	12.3	9.8	12.3
71	0.4	3.0	0.8	1.3	0.4	0.4	0.4	0.8
72	7.1	12.0	4.3	4.9	3.8	5.4	3.3	3.8
73	1.0	3.1	1.0	1.4	1.0	1.2	0.6	0.8
74	3.4	7.1	2.7	3.4	2.0	2.7	2.7	3.0
75	1.8	5.8	1.3	2.4	1.8	1.8	1.3	1.3
76	34.5	81.6	25.1	31.4	18.8	31.4	18.8	25.1
77	72.8	163.8	42.5	60.7	30.3	54.6	36.4	72.8
78	26.9	67.4	19.2	19.2	11.5	19.2	19.2	30.8
79	17.8	38.8	11.3	19.4	9.7	19.4	16.2	21.0
80	33.3	66.6	22.2	33.3	19.4	27.7	25.0	27.7
81	15.9	34.5	11.9	13.3	8.0	13.3	8.0	11.9
82	18.5	40.3	15.1	16.8	10.1	15.1	8.4	10.1
83	18.5	68.5	18.5	16.7	13.0	20.4	14.8	29.6
84	21.3	53.2	18.3	18.3	12.2	18.3	15.2	19.8
85	13.2	35.5	15.2	13.2	9.1	13.2	6.1	4.1
86	20.7	38.8	18.1	18.1	14.2	18.1	9.0	10.3
87	9.2	22.2	9.2	9.2	7.7	7.7	6.1	3.1
88	2.0	6.6	2.6	2.6	2.3	2.3	3.3	2.3
89	11.1	13.6	9.3	9.3	6.2	7.4	4.9	3.1
90	7.7	18.5	6.2	5.4	3.8	6.2	3.1	4.6
91	11.1	23.1	8.3	9.2	6.5	9.2	9.2	11.1
92	10.3	24.1	8.6	9.5	6.9	10.3	6.0	7.7
93	13.0	31.4	9.7	14.1	9.7	14.1	13.0	15.1
94	28.7	33.3	18.2	18.2	15.1	21.2	13.6	19.7
95	4.9	12.2	4.4	5.4	2.9	4.9	3.4	5.4
96	8.4	14.5	4.8	7.2	3.6	4.8	4.8	8.4
97	2.8	7.6	2.1	3.5	1.4	2.8	2.8	2.8
98	10.1	23.6	3.4	6.8	3.4	6.8	3.4	6.8
99	11.5	11.5	4.3	7.2	2.9	4.3	2.9	7.2
100	11.9	11.9	7.9	8.9	5.0	7.9	5.0	6.9
101	8.6	16.3	13.8	12.0	6.9	12.0	12.0	13.8
102	3.8	3.2	2.2	2.2	1.1	2.2	2.2	2.2

S-#	VF5-13	VD5-1	VD5-2	VD5-3	VD5-4	VD5-5	VD5-6	VD5-7
1	2.8	17.4	5.0	14.9	2.5	2.5	2.5	12.4
2	6.4	80.1	16.9	38.0	4.2	12.7	12.7	21.1
3	12.0	62.0	10.8	27.0	5.4	8.1	10.8	24.3
4	3.7	27.5	6.4	21.2	nd	4.2	4.2	12.7
5	0.3	2.2	0.7	1.5	nd	nd	nd	0.7
6	nd	2.7	0.9	3.6	nd	nd	nd	nd
7	0.8	1.3	0.6	0.6	nd	nd	0.6	nd
8	1.5	9.9	1.2	9.9	1.2	2.5	2.5	3.7
9	0.7	5.8	1.7	2.5	0.8	2.1	1.2	1.7
10	3.8	23.1	4.6	16.2	3.5	5.8	4.6	6.9
11	2.8	20.7	6.9	20.7	nd	6.9	3.5	10.4
12	3.2	13.7	1.7	17.1	nd	3.4	1.7	3.4
13	8.1	32.6	5.2	26.1	5.2	7.8	2.6	5.2
14	5.0	23.2	2.8	14.9	3.7	5.6	2.8	4.6
15	11.7	15.8	7.9	15.8	7.9	11.8	5.9	7.9
16	5.9	37.7	4.0	24.3	4.0	5.4	2.7	10.8
17	3.5	8.6	6.9	6.9	6.9	3.4	5.2	8.6
18	2.0	11.7	1.9	15.6	nd	1.9	7.8	nd
19	4.3	10.6	5.3	10.6	nd	nd	nd	nd
20	6.9	11.0	4.4	13.2	nd	nd	nd	nd
21	7.8	16.9	2.1	29.6	nd	4.2	nd	nd
22	3.3	16.9	6.1	15.3	3.1	4.6	4.6	6.1
23	5.3	54.6	13.2	33.1	5.0	8.3	13.2	21.5
24	11.3	80.2	22.5	50.1	15.0	12.5	20.0	27.6
25	8.3	57.8	9.6	32.1	4.8	8.0	8.0	12.8
26	nd	2.8	nd	2.8	0.9	0.9	0.9	2.8
27	0.9	1.5	0.4	2.2	nd	0.4	0.7	0.7
28	1.9	8.1	0.8	6.5	0.8	1.6	0.8	3.2
29	2.0	8.9	4.5	8.9	1.5	nd	1.5	5.9
30	4.3	6.7	1.3	6.7	nd	nd	nd	5.4
31	nd	9.7	nd	9.7	nd	nd	nd	6.5
32	1.2	6.1	2.0	4.1	nd	1.0	1.0	3.1
33	0.3	2.7	nd	2.7	nd	nd	nd	1.4
34	nd	nd	nd	4.3	nd	nd	nd	4.3
35	nd	1.5	0.7	2.2	nd	nd	0.7	3.0
36	0.7	2.4	0.8	2.4	nd	nd	nd	nd
37	1.0	6.9	0.9	3.5	1.7	0.9	2.6	1.7
38	nd	13.3	3.3	10.0	1.7	1.7	3.3	3.3
39	3.2	133.9	39.4	47.3	7.9	15.8	31.5	15.8
40	nd	3.0	nd	3.0	nd	nd	nd	nd
41	nd	11.7	2.3	9.3	nd	nd	2.3	7.0
42	5.3	46.8	4.3	10.6	4.3	6.4	6.4	8.5
43	2.1	24.2	3.5	20.8	nd	3.5	3.5	5.2
44	0.9	8.8	2.5	8.8	1.3	1.3	2.5	nd
45	0.9	16.2	6.1	16.2	nd	2.0	4.1	4.1
46	nd	15.7	1.4	14.3	nd	2.9	1.4	2.9
47	nd	1.6	nd	4.0	nd	nd	nd	nd
48	1.6	7.5	1.9	5.6	nd	nd	nd	nd
49	4.1	nd	nd	nd	nd	nd	nd	nd
50	3.3	7.6	nd	nd	nd	nd	nd	nd
51	7.9	27.2	13.6	16.3	4.1	5.4	10.9	5.4
52	2.5	52.7	32.9	26.4	9.9	13.2	26.4	8.2

S-#	VF5-13	VD5-1	VD5-2	VD5-3	VD5-4	VD5-5	VD5-6	VD5-7
53	nd	3.0	nd	4.6	nd	nd	nd	nd
54	6.7	5.1	1.3	2.5	nd	1.9	1.3	1.9
55	3.1	17.5	3.5	18.6	3.5	2.3	3.5	4.7
56	nd	5.6	2.1	7.0	0.7	0.7	1.4	1.4
57	1.7	7.9	1.8	4.2	0.9	1.2	1.5	1.2
58	3.2	3.1	0.6	1.5	0.2	0.4	0.4	0.8
59	4.5	9.7	2.1	4.1	1.8	1.8	2.1	3.5
60	nd	34.0	5.5	16.6	4.6	5.5	5.5	5.5
61	6.4	9.8	1.6	4.4	1.1	1.6	1.6	2.2
62	1.2	4.3	0.8	2.7	0.5	0.8	0.5	1.3
63	1.1	36.5	4.6	54.8	nd	18.3	4.6	27.4
64	1.1	29.8	3.3	46.4	6.6	13.3	3.3	19.9
65	3.3	73.2	nd	170.7	24.4	36.6	nd	48.8
66	1.1	23.9	2.7	42.5	2.7	10.6	nd	15.9
67	0.8	25.9	3.7	59.1	3.7	14.8	3.7	18.5
68	1.0	24.7	2.7	38.4	nd	8.2	nd	13.7
69	1.8	12.9	1.3	5.1	1.3	3.5	1.3	7.1
70	2.5	11.8	2.0	10.5	2.6	3.9	1.3	7.2
71	0.4	5.9	nd	13.4	3.0	4.5	nd	7.4
72	1.1	5.8	nd	10.1	2.9	3.6	1.4	6.5
73	0.3	1.9	0.3	1.8	nd	0.6	0.2	2.0
74	0.7	4.2	0.9	2.8	nd	0.5	nd	3.7
75	0.4	5.7	1.1	4.0	0.6	1.4	1.1	2.9
76	3.1	15.5	1.6	7.0	1.2	2.3	1.6	5.4
77	6.1	17.3	3.0	7.4	1.7	3.0	3.5	5.2
78	3.8	18.7	2.0	7.9	1.0	2.5	2.0	5.9
79	6.5	11.9	3.2	4.8	2.0	2.4	3.2	4.0
80	2.8	16.1	2.5	6.2	1.2	2.5	2.5	3.7
81	2.7	17.0	3.1	7.0	1.2	2.3	2.3	7.7
82	1.7	14.2	3.3	4.6	1.3	1.7	2.1	2.1
83	3.7	22.2	4.3	8.7	1.6	3.2	3.8	5.9
84	3.0	14.2	2.8	5.7	1.6	2.0	2.4	3.2
85	nd	128.0	48.8	36.6	12.2	12.2	30.5	36.6
86	3.9	59.4	10.5	28.0	8.7	14.0	7.0	34.9
87	1.5	40.8	nd	20.4	6.4	7.7	1.3	25.5
88	nd	22.4	nd	20.0	2.4	6.4	3.2	25.6
89	1.2	21.9	nd	16.4	nd	3.7	nd	19.2
90	0.8	6.3	0.6	4.0	0.8	1.2	0.8	2.9
91	1.8	11.2	2.5	6.7	2.0	2.8	2.8	5.0
92	1.7	7.2	1.2	3.8	0.9	1.2	1.0	2.8
93	2.2	7.8	1.2	4.5	1.0	1.6	1.6	3.9
94	6.1	13.0	1.7	6.1	1.7	2.6	2.2	4.8
95	0.5	4.7	nd	8.1	0.5	1.9	nd	5.7
96	nd	5.6	nd	10.2	0.9	2.3	nd	6.5
97	0.7	4.0	0.9	7.5	0.6	1.7	nd	5.8
98	nd	7.9	1.3	13.1	1.3	2.6	nd	10.5
99	1.4	6.0	0.4	9.4	0.4	3.0	nd	9.4
100	nd	6.3	1.9	4.4	0.6	0.3	1.3	2.5
101	3.4	9.5	1.7	5.1	1.0	1.0	1.4	3.4
102	nd	2.3	0.7	1.9	0.7	0.5	nd	1.2

S-#	VD5-8	VD5-9	VD5-10	VF6-1	VF6-2	VF6-3	VF6-4	VF6-5
1	1.2	1.2	nd	0.6	3.4	9.7	0.3	1.1
2	6.3	2.1	nd	3.0	26.6	74.0	5.9	8.9
3	2.7	nd	nd	2.7	15.1	60.4	5.5	9.6
4	2.1	2.1	nd	1.9	6.7	20.6	1.4	2.9
5	nd	nd	nd	0.6	1.7	8.1	0.4	3.2
6	nd	nd	nd	1.2	3.1	12.8	1.2	3.4
7	nd	nd	nd	0.8	1.6	4.4	0.9	1.6
8	1.2	0.7	nd	0.8	2.1	6.7	1.3	7.5
9	1.7	0.8	0.8	1.0	1.4	9.5	1.4	6.1
10	4.6	2.3	1.2	0.3	2.0	20.9	1.5	12.0
11	nd	nd	nd	nd	10.6	63.7	7.1	28.3
12	3.4	1.7	nd	3.3	11.4	35.8	3.3	8.1
13	5.2	1.3	nd	9.3	14.9	82.0	1.9	22.4
14	4.6	0.9	nd	7.7	19.3	90.8	3.9	21.3
15	nd	nd	nd	nd	nd	nd	nd	nd
16	1.3	nd	nd	nd	3.1	20.8	3.1	4.2
17	nd	nd	nd	nd	nd	19.9	2.5	13.7
18	nd	nd	nd	nd	2.3	18.3	2.3	11.4
19	nd	nd	nd	nd	nd	nd	nd	nd
20	nd	nd	nd	nd	11.1	19.4	8.3	13.9
21	nd	nd	nd	nd	12.1	24.2	nd	nd
22	3.1	1.5	nd	nd	14.2	49.6	4.7	3.5
23	6.6	5.0	1.7	8.3	29.2	98.1	8.3	8.3
24	10.0	10.0	5.0	2.5	30.4	106.6	12.7	10.1
25	6.4	4.8	1.6	3.5	29.3	77.7	6.9	5.2
26	nd	nd	nd	nd	nd	3.5	nd	nd
27	0.4	nd	nd	nd	nd	0.9	nd	nd
28	0.8	nd	nd	0.3	0.3	8.3	nd	0.5
29	nd	nd	nd	nd	3.8	6.8	nd	nd
30	nd	nd	nd	0.9	7.3	12.3	0.9	1.8
31	1.6	nd	nd	nd	6.1	10.8	nd	4.2
32	nd	nd	nd	0.2	2.1	9.2	1.4	1.8
33	nd	nd	nd	nd	0.4	1.5	nd	nd
34	nd	nd	nd	nd	nd	2.1	nd	nd
35	nd	nd	nd	nd	0.5	1.4	nd	nd
36	nd	nd	nd	nd	nd	4.6	nd	nd
37	0.9	nd	nd	0.1	1.7	3.0	0.1	0.2
38	nd	nd	nd	nd	0.6	6.1	nd	nd
39	15.8	15.8	nd	nd	5.8	31.0	1.9	15.5
40	nd	nd	nd	nd	nd	15.6	nd	nd
41	nd	nd	nd	nd	1.1	12.0	nd	nd
42	4.3	2.1	2.1	1.9	24.8	87.7	3.8	11.4
43	1.7	nd	nd	1.7	12.5	35.1	1.7	5.0
44	nd	nd	nd	nd	6.3	26.4	1.9	4.4
45	2.0	2.0	1.2	0.6	5.9	25.8	1.8	4.7
46	1.4	nd	nd	0.5	4.4	24.1	2.2	5.5
47	nd	nd	nd	nd	7.7	23.9	nd	1.5
48	nd	nd	nd	nd	5.8	22.1	1.7	6.4
49	nd	nd	nd	1.6	8.6	25.8	3.1	9.4
50	nd	nd	nd	1.5	8.9	29.7	2.2	8.2
51	5.4	2.7	2.7	2.8	39.8	128.1	11.4	34.2
52	13.2	6.6	6.6	nd	12.1	60.4	7.6	24.2

S-#	VD5-8	VD5-9	VD5-10	VF6-1	VF6-2	VF6-3	VF6-4	VF6-5
53	nd	nd	nd	nd	11.7	32.8	nd	2.3
54	nd	nd	nd	2.4	15.9	50.1	3.7	11.0
55	1.2	nd	nd	nd	5.2	41.8	1.0	12.5
56	0.7	0.7	nd	1.0	8.2	43.1	3.1	13.3
57	0.6	nd	nd	1.0	10.5	43.8	2.9	9.5
58	0.2	0.1	nd	nd	7.1	27.1	1.4	4.3
59	1.2	0.6	0.3	nd	11.0	36.6	2.7	9.2
60	2.8	1.8	0.9	0.8	8.8	33.6	3.2	5.6
61	0.5	nd	nd	nd	18.4	52.6	3.9	7.9
62	0.3	0.3	nd	nd	4.3	15.1	1.1	4.3
63	nd	nd	nd	nd	6.0	29.8	1.5	7.5
64	3.3	nd	nd	0.5	6.8	19.8	2.1	3.1
65	7.3	nd	nd	2.8	8.5	28.2	3.8	4.7
66	2.7	nd	nd	nd	2.2	13.1	1.1	2.2
67	3.7	nd	nd	nd	nd	5.1	nd	2.2
68	2.7	nd	nd	nd	1.6	11.1	1.6	2.0
69	nd	nd	nd	0.4	5.0	12.1	0.8	2.5
70	1.3	nd	nd	0.4	4.4	11.6	0.7	2.5
71	nd	nd	nd	nd	nd	nd	nd	nd
72	nd	nd	nd	0.4	1.2	3.0	0.4	0.6
73	nd	nd	nd	0.1	0.5	1.4	nd	0.2
74	nd	nd	nd	nd	1.8	6.4	1.1	3.6
75	0.9	nd	nd	nd	0.9	2.5	0.3	1.3
76	1.6	1.2	0.4	2.3	19.7	46.4	2.3	2.3
77	1.7	1.3	0.9	22.5	63.8	165.2	7.5	22.5
78	1.0	0.5	nd	2.6	23.3	59.5	5.2	7.8
79	1.6	0.8	nd	0.9	10.7	35.5	2.7	12.4
80	1.2	nd	nd	nd	12.7	40.2	2.1	8.5
81	0.8	0.4	nd	0.9	9.4	19.7	0.9	2.8
82	1.3	0.8	nd	1.1	4.5	11.2	0.4	3.0
83	1.6	1.1	0.5	0.5	12.3	32.4	3.1	4.6
84	0.8	nd	nd	0.6	9.1	22.7	1.7	2.8
85	12.2	nd	nd	1.0	3.8	7.2	1.7	3.8
86	7.0	3.5	nd	nd	1.2	3.9	nd	0.4
87	nd	nd	nd	nd	nd	nd	nd	nd
88	1.6	1.6	nd	0.5	0.8	3.2	1.0	3.9
89	nd	nd	nd	nd	nd	1.4	nd	0.8
90	0.4	nd	nd	nd	1.6	4.3	nd	1.3
91	2.0	1.1	0.6	1.8	9.7	25.4	2.4	4.8
92	0.7	0.3	nd	0.7	3.6	9.4	0.7	1.5
93	1.0	0.4	0.2	0.4	6.3	17.9	1.7	1.7
94	1.7	0.9	nd	nd	6.1	26.8	3.8	2.3
95	nd	0.7	nd	nd	3.7	4.1	nd	nd
96	nd	nd	nd	nd	5.0	6.7	nd	1.7
97	0.6	nd	nd	nd	2.1	5.3	nd	2.8
98	nd	nd	nd	nd	7.1	14.2	nd	5.3
99	nd	nd	nd	nd	4.1	5.9	0.6	3.6
100	nd	nd	nd	nd	5.3	21.1	1.1	4.2
101	1.0	nd	nd	nd	6.6	22.5	1.3	5.3
102	0.5	nd	nd	nd	2.2	2.5	nd	nd

S-#	VF6-6	VF6-7	VF6-8	VF6-9	VF6-10	VF6-11	VF6-12	VD6-1
1	5.7	4.6	0.6	nd	2.3	0.6	5.7	7.3
2	35.5	23.7	5.9	3.0	11.8	1.5	5.9	40.0
3	39.8	24.7	5.5	4.1	12.4	1.4	8.2	25.0
4	9.6	7.7	1.4	1.0	4.3	nd	2.4	11.3
5	1.9	1.7	0.4	0.2	1.9	0.2	0.9	7.2
6	2.4	2.1	nd	nd	2.1	nd	nd	7.6
7	1.3	1.1	0.1	nd	0.5	nd	nd	3.8
8	6.3	3.8	1.7	1.7	8.4	0.4	1.7	17.0
9	5.1	4.1	2.0	1.0	5.5	0.3	1.7	14.4
10	19.9	12.5	4.5	4.0	19.9	1.0	4.5	30.2
11	14.2	14.2	10.6	7.1	46.0	2.1	7.1	30.5
12	14.7	13.0	3.3	1.6	16.3	1.0	3.3	15.9
13	13.0	11.2	3.7	3.7	26.1	1.1	5.6	49.3
14	15.5	15.5	3.9	3.9	19.3	1.2	3.9	34.2
15	10.1	12.6	7.6	7.6	22.7	nd	nd	42.7
16	39.4	20.8	8.3	3.1	25.9	1.0	7.3	27.4
17	14.9	9.9	5.0	2.5	9.9	nd	nd	31.7
18	16.0	9.2	6.9	2.3	13.7	nd	nd	28.4
19	nd	nd	nd	nd	nd	nd	nd	28.9
20	19.4	18.0	6.9	5.6	15.3	nd	nd	27.4
21	19.7	16.7	12.1	3.0	12.1	nd	9.1	39.8
22	26.0	18.9	4.7	2.4	11.8	0.7	3.5	24.4
23	50.1	37.6	8.3	4.2	29.2	2.1	6.3	50.0
24	60.9	40.6	7.6	5.1	20.3	2.5	7.6	42.7
25	34.5	22.4	5.2	1.7	12.1	1.0	3.5	19.1
26	2.2	1.6	nd	nd	1.4	nd	2.2	3.7
27	0.3	nd	nd	nd	0.2	nd	0.2	nd
28	4.0	2.5	0.5	nd	1.5	0.8	0.5	2.2
29	4.9	2.7	nd	nd	1.4	nd	2.5	1.1
30	9.1	4.6	nd	nd	1.8	0.9	5.5	10.7
31	5.6	2.8	nd	nd	nd	nd	nd	6.1
32	4.8	3.7	1.2	0.7	2.1	nd	1.4	5.0
33	1.6	1.5	nd	nd	1.2	0.6	1.8	nd
34	3.0	1.7	nd	nd	2.6	0.8	3.8	1.9
35	2.5	2.7	0.7	0.2	2.7	1.8	5.2	nd
36	0.6	0.6	nd	nd	nd	nd	nd	nd
37	1.6	1.3	nd	nd	0.3	nd	nd	1.7
38	2.4	1.8	nd	nd	0.6	nd	0.6	5.7
39	20.3	19.4	1.9	nd	12.6	nd	14.5	53.5
40	14.9	14.2	nd	nd	nd	nd	nd	nd
41	8.7	3.3	nd	nd	nd	nd	nd	8.8
42	40.0	28.6	7.6	5.7	21.0	3.8	5.7	24.5
43	18.4	12.5	3.3	2.5	10.0	0.8	2.5	17.7
44	8.8	6.3	1.9	1.3	4.4	nd	0.6	34.9
45	10.5	7.0	2.3	1.2	5.3	nd	1.2	31.6
46	9.9	6.6	2.2	1.6	3.8	nd	0.5	10.0
47	10.8	7.7	nd	nd	6.2	nd	nd	4.4
48	7.6	5.8	1.2	0.6	5.2	0.6	2.3	22.2
49	7.0	7.0	nd	nd	6.3	nd	nd	20.5
50	6.7	6.7	0.7	0.7	6.7	nd	nd	11.9
51	39.8	34.2	5.7	5.7	19.9	1.7	5.7	150.7
52	13.6	12.1	1.5	1.5	12.1	nd	nd	200.5

S-#	VF6-6	VF6-7	VF6-8	VF6-9	VF6-10	VF6-11	VF6-12	VD6-1
53	2.3	2.3	nd	nd	nd	nd	nd	13.8
54	13.4	11.0	2.4	2.4	7.3	nd	1.2	16.8
55	6.3	4.2	1.0	nd	4.2	nd	nd	49.1
56	9.2	8.2	1.0	2.1	5.1	nd	2.1	35.7
57	10.5	7.6	1.9	1.9	4.8	nd	1.0	33.5
58	7.1	5.0	1.4	nd	nd	nd	nd	10.0
59	13.7	8.2	1.8	0.9	4.6	nd	nd	20.2
60	12.8	9.6	2.4	1.6	4.0	0.5	1.6	17.6
61	18.4	13.2	3.9	2.6	3.9	nd	nd	17.8
62	5.4	3.2	nd	nd	nd	nd	nd	6.0
63	10.4	7.5	1.5	1.5	6.0	0.7	1.5	18.1
64	7.3	5.2	1.0	0.5	7.8	1.0	2.1	7.1
65	10.4	8.5	nd	1.9	4.7	nd	nd	9.9
66	5.8	4.4	1.1	0.7	1.5	0.7	1.5	4.8
67	3.7	2.2	nd	1.5	3.7	nd	nd	2.2
68	5.1	3.9	1.2	0.8	2.4	nd	nd	4.0
69	4.2	3.3	nd	nd	0.4	nd	1.7	4.9
70	4.4	3.6	0.7	nd	1.5	0.4	1.5	7.1
71	nd	nd	nd	nd	nd	nd	nd	nd
72	1.2	1.6	0.4	0.4	0.6	0.4	0.6	0.5
73	0.8	0.8	nd	0.2	0.4	nd	nd	0.4
74	4.6	4.3	nd	nd	nd	nd	nd	6.2
75	1.6	0.9	0.6	0.3	1.3	nd	nd	2.4
76	17.4	11.6	2.3	0.7	3.5	nd	2.3	6.1
77	56.3	37.5	7.5	3.8	22.5	2.3	7.5	25.3
78	24.6	15.5	3.9	1.3	12.9	nd	2.6	15.0
79	10.7	8.0	2.7	1.8	6.2	0.9	1.8	15.5
80	13.8	10.6	1.1	nd	4.2	nd	1.1	13.2
81	5.6	3.7	0.5	0.3	1.9	nd	0.5	10.5
82	4.5	3.4	0.7	nd	0.7	nd	0.7	5.9
83	15.4	9.3	1.5	0.8	6.2	0.8	1.5	22.2
84	10.8	6.8	1.7	0.6	2.3	0.6	1.1	7.3
85	3.8	3.8	1.0	nd	nd	nd	0.7	12.8
86	2.8	1.8	0.4	nd	nd	nd	nd	1.3
87	nd	nd	nd	nd	nd	nd	nd	0.5
88	2.9	1.5	0.5	nd	0.3	nd	nd	4.1
89	1.2	0.6	0.4	nd	nd	nd	nd	0.6
90	1.3	0.8	nd	nd	nd	nd	nd	3.0
91	9.7	6.0	1.2	0.6	2.4	nd	1.2	13.8
92	3.6	2.2	0.5	0.1	0.5	nd	nd	2.9
93	7.9	5.4	1.3	0.8	2.5	0.3	0.8	3.9
94	11.5	10.0	2.3	nd	3.1	nd	nd	6.1
95	2.3	0.9	0.7	nd	nd	nd	nd	1.1
96	3.3	1.3	nd	nd	nd	nd	nd	3.2
97	2.5	1.1	nd	nd	nd	nd	nd	2.8
98	3.6	1.8	0.9	0.9	1.8	nd	nd	8.0
99	1.2	0.6	nd	nd	nd	nd	nd	3.8
100	4.7	4.2	0.5	nd	1.6	nd	nd	4.7
101	10.6	7.9	1.3	1.3	4.0	nd	nd	7.5
102	1.9	0.6	nd	nd	nd	nd	nd	1.3

S-#	VD6-2	VD6-3	VD6-4	VD6-5	VD6-6	VD6-7	VF7-1	VF7-2
1	6.6	8.8	0.7	9.5	4.4	2.2	4.0	0.5
2	40.0	48.4	5.3	8.4	12.6	8.4	8.3	1.2
3	27.7	33.3	2.8	11.1	10.2	6.5	10.9	0.7
4	11.0	12.4	1.4	4.9	3.2	2.1	3.8	0.5
5	3.8	10.7	nd	1.4	3.5	1.2	3.1	nd
6	3.8	10.3	0.5	2.4	3.8	1.3	2.5	nd
7	3.2	4.3	0.5	1.0	1.6	0.6	1.0	nd
8	17.0	21.3	2.1	3.5	5.7	2.8	4.8	0.5
9	10.8	18.5	1.5	3.6	6.2	2.6	2.9	0.5
10	35.2	36.9	3.4	6.7	11.7	5.0	10.8	0.8
11	30.5	45.7	10.2	15.2	22.8	10.2	45.0	5.6
12	14.3	23.8	3.2	5.6	6.4	4.8	13.9	1.7
13	64.7	58.5	4.6	9.2	21.6	6.2	22.3	1.3
14	55.7	40.5	2.5	7.6	15.2	6.3	20.0	1.5
15	21.4	47.0	12.8	8.5	14.9	10.7	12.5	nd
16	65.1	44.5	13.7	6.9	13.7	13.7	24.9	4.2
17	25.3	28.5	12.7	14.3	17.4	11.1	11.4	nd
18	15.5	25.9	2.6	12.9	12.9	7.8	9.7	nd
19	14.5	28.9	9.6	9.6	9.6	12.8	3.9	nd
20	9.1	24.3	nd	nd	nd	9.1	4.5	nd
21	57.8	43.4	14.5	18.1	21.7	10.8	3.7	nd
22	16.6	29.7	5.2	7.0	7.9	7.0	11.7	1.5
23	56.2	71.8	9.4	15.6	21.9	17.2	19.8	1.9
24	51.2	59.7	13.7	13.7	17.1	17.1	28.4	1.9
25	18.4	19.7	2.6	5.3	6.6	7.2	10.6	1.6
26	1.9	2.5	nd	2.5	1.2	nd	3.1	nd
27	nd	nd	nd	nd	nd	nd	nd	nd
28	5.6	3.3	nd	1.4	nd	0.6	0.7	nd
29	4.2	5.8	nd	3.7	nd	nd	nd	nd
30	6.6	14.8	nd	11.5	8.2	1.6	4.9	nd
31	12.1	20.6	nd	nd	9.7	10.9	nd	nd
32	3.8	7.9	0.2	2.0	2.7	1.8	1.9	nd
33	1.5	2.2	nd	2.6	1.1	nd	2.3	0.1
34	nd	3.4	nd	4.8	1.9	nd	2.9	nd
35	nd	nd	nd	5.0	1.3	1.0	3.5	nd
36	nd	nd	nd	nd	nd	nd	nd	nd
37	2.2	2.4	nd	0.3	0.3	nd	0.3	nd
38	2.8	6.4	nd	2.1	2.1	nd	0.5	nd
39	24.7	69.9	20.6	20.6	24.7	4.1	0.4	nd
40	nd	nd	nd	nd	nd	nd	nd	nd
41	6.6	16.1	nd	nd	nd	nd	nd	nd
42	35.0	35.0	6.1	7.0	10.5	8.8	18.6	0.6
43	30.5	28.1	5.6	4.8	9.6	5.6	11.6	nd
44	14.2	55.6	6.5	5.2	19.4	10.3	11.1	0.3
45	11.7	51.5	7.0	5.8	16.4	7.0	11.4	0.7
46	14.1	14.1	4.2	2.5	4.2	2.5	7.4	nd
47	7.0	14.9	nd	nd	nd	nd	9.7	nd
48	16.2	28.1	4.4	6.6	8.9	7.4	15.5	1.0
49	8.4	20.5	nd	2.8	10.3	nd	20.7	nd
50	10.7	15.4	nd	2.4	7.1	1.2	11.9	nd
51	53.8	253.0	26.9	37.7	75.4	48.5	13.1	0.8
52	56.1	368.9	32.1	48.1	96.2	56.1	11.9	nd

S-#	VD6-2	VD6-3	VD6-4	VD6-5	VD6-6	VD6-7	VF7-1	VF7-2
53	2.8	22.1	nd	nd	nd	nd	14.1	nd
54	14.2	22.6	2.6	7.1	7.7	5.2	10.5	nd
55	28.6	54.5	6.8	6.8	15.0	8.2	3.8	nd
56	11.9	43.6	9.9	5.0	11.9	6.0	11.2	0.9
57	12.0	37.8	12.0	5.2	10.3	5.2	16.7	2.6
58	5.7	9.5	1.7	1.9	2.8	1.2	5.3	nd
59	13.1	21.2	2.5	3.0	5.5	2.0	7.4	1.2
60	13.4	19.2	1.7	3.3	5.0	1.7	6.2	0.4
61	11.4	14.6	2.7	3.7	3.7	2.7	8.1	0.7
62	4.5	6.6	0.6	0.9	1.2	0.9	nd	nd
63	39.9	22.8	1.0	3.8	9.5	3.8	10.2	1.1
64	25.6	11.4	1.4	3.6	4.3	3.6	12.8	2.9
65	93.7	14.8	2.5	9.9	12.3	4.9	0.8	0.1
66	25.3	7.2	0.6	2.4	3.6	1.8	3.9	0.7
67	21.8	6.5	nd	2.2	1.5	nd	3.2	nd
68	19.1	6.9	1.2	2.3	3.5	1.2	3.8	nd
69	11.0	7.6	4.6	3.0	3.0	1.1	4.7	nd
70	13.4	7.9	3.2	2.4	3.9	1.6	4.6	nd
71	nd	11.2	1.2	1.6	0.8	0.4	nd	nd
72	0.5	7.5	1.0	0.8	1.0	0.8	nd	nd
73	1.4	2.4	nd	0.3	0.1	nd	2.1	nd
74	6.2	6.6	0.8	1.6	2.3	0.8	1.6	nd
75	3.1	4.4	0.9	1.1	1.5	0.9	2.5	nd
76	7.0	7.0	1.8	2.6	2.6	1.2	4.9	nd
77	16.5	38.9	4.9	3.9	9.7	2.9	53.5	7.6
78	21.5	18.3	2.1	2.1	4.8	3.2	29.1	2.9
79	7.7	19.4	1.3	5.2	5.2	2.6	12.3	0.8
80	9.9	16.5	1.1	3.3	11.5	2.2	17.1	1.7
81	18.5	11.4	2.6	1.8	2.6	1.8	4.5	0.3
82	3.5	8.8	1.2	0.9	2.6	0.6	1.8	nd
83	20.8	28.4	2.8	4.2	6.9	4.2	7.7	0.7
84	6.0	7.5	1.0	1.0	2.5	0.8	5.3	0.6
85	9.9	11.7	1.8	1.5	2.6	1.5	1.7	0.1
86	7.5	3.7	nd	0.5	0.8	nd	nd	nd
87	5.0	3.7	0.7	1.4	nd	0.5	0.9	nd
88	11.0	12.3	2.7	2.7	4.1	2.1	5.5	1.3
89	5.9	5.3	0.9	1.2	0.6	nd	3.1	nd
90	4.2	5.0	0.6	1.0	1.6	0.4	3.3	0.3
91	9.6	18.4	1.8	2.8	5.5	2.8	6.4	0.7
92	3.6	3.9	0.4	0.6	1.2	0.6	1.5	0.1
93	5.2	5.1	0.4	1.0	1.6	0.9	3.6	0.5
94	8.1	10.2	2.0	3.6	3.6	2.5	7.1	nd
95	6.7	1.7	nd	0.6	0.8	0.3	0.5	nd
96	10.3	4.5	1.3	1.9	2.6	nd	5.7	nd
97	6.3	4.9	0.7	0.7	2.1	0.7	3.3	nd
98	16.1	11.5	nd	2.3	4.6	2.3	10.7	nd
99	7.6	6.9	0.7	1.0	2.1	0.7	3.2	nd
100	5.5	6.2	0.7	1.5	4.4	2.2	3.6	nd
101	8.9	12.1	4.7	1.9	6.5	1.4	10.6	2.3
102	3.0	3.4	0.7	2.0	1.7	1.3	2.6	nd

S-#	VF7-3	VF7-4	VD7-1	VD7-2	VF8	VD8	PF4-1	PF4-2
1	1.0	0.7	nd	13.1	4.9	nd	3.7	7.4
2	3.2	1.2	13.9	10.4	3.3	nd	1.9	3.7
3	3.6	1.1	14.7	19.1	5.6	2.3	23.1	3.6
4	1.9	0.5	7.9	14.5	3.6	nd	1.8	4.6
5	3.6	0.4	14.4	26.2	2.6	14.7	nd	nd
6	3.0	0.4	11.3	19.3	3.1	32.4	nd	nd
7	3.0	nd	nd	5.9	nd	nd	nd	nd
8	10.6	1.5	60.0	48.0	3.5	31.3	nd	nd
9	3.6	1.1	34.2	25.6	3.8	nd	nd	nd
10	9.2	2.0	48.5	39.3	2.0	nd	nd	nd
11	33.8	nd	122.4	113.6	24.9	87.0	nd	nd
12	7.5	2.3	47.9	43.5	10.6	15.8	nd	nd
13	15.1	3.3	106.9	91.1	6.3	8.6	0.4	1.3
14	13.0	2.0	73.9	59.1	3.8	nd	1.4	2.8
15	21.4	nd	24.2	36.3	nd	nd	nd	nd
16	11.1	4.8	57.1	43.9	9.4	1.4	nd	nd
17	14.1	nd	22.0	31.5	nd	nd	nd	nd
18	6.4	nd	13.3	nd	nd	2.1	nd	nd
19	5.3	nd	nd	nd	nd	0.2	nd	nd
20	2.2	nd	nd	nd	nd	18.6	nd	nd
21	1.9	nd	nd	nd	nd	nd	nd	nd
22	2.8	1.8	16.8	12.0	2.9	nd	8.7	9.4
23	6.6	1.9	37.8	36.8	2.8	nd	2.6	1.7
24	11.3	nd	39.0	19.5	2.7	nd	4.5	9.1
25	3.7	1.2	12.5	9.4	2.6	nd	2.9	4.7
26	nd	nd	nd	nd	4.5	nd	nd	nd
27	nd	nd	nd	nd	12.5	nd	nd	5.4
28	0.6	0.4	nd	nd	1.9	nd	nd	nd
29	nd	nd	nd	nd	1.1	nd	nd	nd
30	nd	nd	nd	nd	0.7	nd	nd	nd
31	nd	nd	nd	nd	1.6	nd	nd	nd
32	0.8	nd	8.9	12.5	2.8	nd	nd	nd
33	1.4	0.8	4.3	7.8	3.7	nd	1.6	7.8
34	nd	nd	nd	nd	5.9	1.4	nd	4.3
35	nd	2.5	nd	nd	6.1	nd	nd	5.1
36	nd	nd	nd	nd	nd	nd	1.5	3.7
37	0.3	nd	0.5	1.3	0.5	nd	0.2	1.0
38	0.5	nd	nd	nd	nd	nd	0.4	2.6
39	nd	0.1	0.9	1.2	0.7	nd	nd	3.7
40	nd	nd	nd	nd	nd	nd	nd	nd
41	nd	nd	nd	nd	nd	nd	nd	nd
42	8.1	nd	25.4	25.4	nd	nd	1.2	0.8
43	6.3	nd	24.3	22.0	nd	nd	0.6	4.6
44	8.7	nd	58.5	58.5	nd	25.6	0.2	7.2
45	7.8	1.0	55.9	50.1	0.7	17.4	nd	0.2
46	5.7	nd	17.5	16.7	1.1	nd	1.2	3.6
47	1.5	nd	8.4	9.5	nd	nd	nd	3.9
48	10.3	1.5	29.2	37.2	nd	15.0	nd	nd
49	18.2	nd	nd	nd	nd	51.6	nd	nd
50	10.2	nd	13.0	18.3	nd	86.0	nd	nd
51	10.4	0.8	93.7	110.3	2.4	113.0	1.5	4.5
52	17.2	nd	201.1	238.9	nd	87.0	nd	nd

S-#	VF7-3	VF7-4	VD7-1	VD7-2	VF8	VD8	PF4-1	PF4-2
53	1.9	nd	nd	nd	nd	96.0	2.0	3.0
54	9.0	0.3	25.1	26.2	1.4	38.7	nd	nd
55	7.6	nd	152.5	91.5	13.7	151.0	0.5	5.4
56	12.5	0.9	174.4	142.7	3.8	146.0	0.2	3.0
57	14.1	2.6	189.0	153.0	3.8	172.0	0.4	5.5
58	3.0	nd	14.1	12.9	2.8	18.4	nd	2.1
59	4.3	nd	25.3	18.5	4.8	nd	0.3	2.4
60	3.3	nd	26.8	23.8	1.8	16.2	nd	2.7
61	3.0	nd	10.5	10.5	8.2	41.3	0.4	3.1
62	3.0	nd	nd	nd	nd	nd	1.0	2.0
63	5.1	1.7	20.3	21.0	3.9	24.7	2.0	43.5
64	6.6	5.8	28.2	31.3	29.3	165.0	2.4	32.3
65	0.5	0.4	1.7	2.0	2.2	nd	5.3	47.7
66	1.8	1.4	7.5	9.6	11.2	67.6	3.2	35.7
67	3.2	nd	10.9	19.2	20.5	136.0	8.3	48.4
68	1.6	nd	6.5	11.6	14.2	35.5	4.9	26.8
69	1.6	nd	nd	nd	nd	5.2	1.5	7.5
70	1.5	nd	nd	nd	nd	16.8	1.1	9.0
71	nd	nd	nd	nd	nd	0.7	1.6	9.8
72	nd	nd	nd	nd	nd	54.6	nd	7.7
73	0.5	nd	1.1	3.5	10.7	25.0	0.4	2.4
74	0.8	nd	7.2	9.9	12.3	73.0	0.3	1.6
75	2.9	nd	14.2	15.8	7.1	92.0	0.4	1.7
76	0.7	nd	20.2	44.4	8.0	153.0	1.7	1.5
77	15.3	nd	85.0	98.0	18.5	118.0	2.2	4.4
78	11.7	2.2	37.3	31.4	4.2	61.9	1.2	1.2
79	12.3	1.5	53.5	53.5	5.9	277.0	nd	nd
80	9.1	1.1	37.4	37.4	4.9	31.9	0.5	0.5
81	1.9	nd	12.2	9.6	2.0	0.6	0.3	0.4
82	3.3	nd	21.3	24.7	5.6	209.0	0.8	1.9
83	3.3	0.5	20.0	15.5	1.7	nd	1.0	1.5
84	2.0	0.4	15.5	12.3	2.6	79.0	2.8	4.6
85	1.7	0.1	8.2	10.9	1.9	9.1	3.8	5.1
86	nd	nd	nd	nd	0.9	13.5	nd	2.1
87	2.6	nd	7.4	18.4	4.5	294.0	nd	nd
88	9.6	0.8	50.3	69.7	18.4	958.0	10.7	10.7
89	3.8	nd	9.4	25.4	7.6	454.0	11.4	22.7
90	4.0	0.7	38.2	40.1	11.6	658.0	4.3	8.7
91	4.7	0.3	47.8	50.4	10.3	605.0	nd	6.1
92	0.9	0.1	6.5	6.5	2.1	13.7	nd	nd
93	1.5	0.2	8.0	8.3	2.2	8.5	1.4	1.4
94	2.4	nd	13.0	23.8	nd	32.9	nd	1.8
95	0.3	nd	9.3	15.4	18.9	92.0	nd	nd
96	4.0	nd	44.6	37.2	22.2	141.0	nd	nd
97	2.7	nd	34.4	29.4	20.3	172.0	nd	nd
98	9.0	nd	50.0	60.0	25.4	302.0	nd	nd
99	3.7	nd	57.4	54.6	34.3	364.0	nd	nd
100	5.1	nd	22.9	28.9	4.2	104.0	nd	nd
101	6.1	nd	53.4	48.6	4.0	47.1	nd	nd
102	2.4	nd	27.4	22.9	6.1	261.0	nd	nd

S-#	PF4-3	PF4-4	PF4-5	PF4-6	PF4-7	PF4-8	PF4-9	PF4-10
1	22.3	11.1	26.0	29.7	29.7	44.6	22.3	3.7
2	5.6	3.7	7.4	7.4	9.3	13.0	4.6	3.7
3	7.1	3.6	7.1	10.7	19.6	33.8	10.7	10.7
4	4.6	4.6	6.4	7.3	11.0	22.0	3.7	0.9
5	nd	nd	nd	nd	nd	nd	2.1	nd
6	nd	nd	nd	nd	nd	nd	nd	nd
7	nd	nd	nd	1.7	nd	nd	2.8	nd
8	nd	nd	nd	5.2	3.4	24.1	nd	3.4
9	0.5	nd	nd	1.5	2.0	2.5	1.0	0.5
10	nd	nd	nd	2.2	2.7	3.2	1.1	1.1
11	nd	nd	nd	1.2	3.6	4.9	1.8	1.2
12	nd	nd	nd	2.5	5.0	6.2	3.7	1.2
13	1.3	1.3	0.8	1.7	1.9	3.0	1.3	0.6
14	1.8	2.8	2.8	2.3	3.7	4.6	1.8	1.4
15	nd	nd	nd	7.4	8.9	20.7	5.9	5.9
16	nd	nd	nd	7.9	9.8	19.6	5.9	2.0
17	nd	nd	nd	8.3	10.4	12.4	6.2	6.2
18	nd	nd	nd	13.0	9.7	13.0	4.3	4.3
19	nd	nd	nd	2.0	2.9	2.9	2.0	2.5
20	nd	nd	nd	nd	nd	7.6	nd	nd
21	nd	nd	nd	3.2	nd	12.9	nd	nd
22	5.1	7.3	8.7	8.7	11.6	16.7	5.8	5.8
23	10.3	7.7	8.6	8.6	12.9	17.2	2.6	1.7
24	13.6	11.3	13.6	15.9	15.9	28.3	10.2	6.8
25	5.8	4.1	4.7	5.8	7.6	14.0	3.5	1.2
26	nd	nd	nd	4.4	7.8	13.3	2.2	2.2
27	5.4	3.0	5.4	7.2	8.4	14.9	6.0	1.8
28	nd	nd	nd	6.0	nd	6.0	6.0	6.0
29	nd	nd	nd	5.5	3.4	9.6	4.1	0.7
30	nd	nd	nd	2.1	16.5	14.4	5.2	3.1
31	nd	nd	nd	nd	nd	nd	nd	nd
32	nd	nd	nd	1.1	5.4	4.3	nd	nd
33	11.0	9.4	9.4	15.7	25.1	43.9	9.4	4.7
34	7.5	3.2	3.2	8.6	8.6	18.3	4.3	3.2
35	6.3	1.9	5.1	6.3	8.9	14.6	2.5	1.9
36	5.1	4.4	6.6	5.9	7.3	13.2	5.9	2.9
37	1.9	1.2	1.7	2.5	2.1	4.3	1.9	1.2
38	2.6	2.6	2.6	3.5	5.7	10.5	1.8	1.3
39	4.6	1.4	5.1	5.1	5.1	9.2	4.2	1.8
40	nd	nd	nd	nd	nd	nd	nd	nd
41	nd	nd	nd	nd	nd	5.1	nd	nd
42	8.6	4.3	4.3	3.9	3.9	7.0	2.7	0.8
43	2.5	1.5	5.8	3.7	2.5	2.5	1.5	0.8
44	1.0	0.6	1.2	1.2	1.4	1.4	0.2	0.2
45	1.5	0.7	2.0	0.7	0.7	2.4	0.5	0.5
46	3.6	1.8	2.4	2.4	4.2	4.8	1.8	1.2
47	0.7	0.3	1.0	0.8	0.8	0.8	0.3	nd
48	nd	nd	nd	nd	2.3	1.6	0.8	nd
49	nd	nd	nd	nd	nd	1.4	nd	nd
50	nd	nd	nd	5.3	3.5	5.3	7.1	nd
51	4.5	3.8	3.8	4.9	5.3	8.7	1.9	1.1
52	nd	nd	nd	nd	nd	nd	nd	nd

S-#	PF4-3	PF4-4	PF4-5	PF4-6	PF4-7	PF4-8	PF4-9	PF4-10
53	0.7	0.5	0.5	1.0	1.5	1.5	1.5	0.7
54	nd	nd	nd	nd	nd	nd	nd	nd
55	2.7	1.1	2.2	2.4	3.5	4.9	1.4	0.5
56	0.8	0.5	0.8	0.6	1.4	1.1	0.8	0.5
57	0.8	1.3	2.1	0.8	1.7	1.9	0.8	nd
58	2.1	0.7	1.7	3.1	4.9	6.9	1.4	1.4
59	1.3	0.7	1.7	2.7	3.4	5.4	2.7	1.0
60	2.7	1.3	2.7	8.0	12.0	12.0	5.3	6.7
61	2.3	1.6	2.3	3.1	4.7	7.8	2.3	1.2
62	16.0	12.0	6.0	nd	nd	nd	nd	nd
63	5.9	3.0	4.9	3.0	4.0	7.9	2.0	2.0
64	7.9	4.7	6.3	4.7	7.9	12.6	3.1	6.3
65	21.2	10.6	19.1	15.9	21.2	27.6	8.5	4.2
66	11.4	6.5	13.0	9.7	13.0	16.2	4.9	4.1
67	22.1	13.8	16.6	13.8	29.0	49.7	6.9	18.0
68	15.8	9.7	13.4	11.0	24.4	35.3	6.1	3.7
69	8.9	6.0	6.0	8.9	20.9	20.9	10.4	6.0
70	10.1	4.5	9.0	6.7	9.0	18.0	4.5	3.4
71	16.3	9.8	14.7	16.3	22.8	55.5	6.5	4.9
72	10.8	4.6	9.2	9.2	18.5	27.7	4.6	6.2
73	3.1	1.6	2.4	2.2	3.5	7.3	1.4	0.6
74	1.4	0.6	1.3	0.9	1.7	2.3	0.8	0.5
75	2.2	0.6	1.3	1.0	4.0	4.4	1.0	0.5
76	1.2	1.7	0.9	2.0	3.2	4.4	1.2	1.2
77	4.9	3.8	5.5	5.5	6.6	12.0	2.7	1.1
78	3.0	1.8	2.4	2.4	3.6	6.5	0.9	0.6
79	nd	nd	nd	0.6	1.9	2.5	1.9	1.2
80	1.4	0.9	1.4	1.8	2.5	3.7	0.9	0.7
81	0.8	0.3	0.5	0.8	1.0	1.6	0.4	0.3
82	3.0	1.1	2.3	2.3	4.6	5.7	1.9	0.8
83	2.4	1.5	2.9	2.9	5.8	9.7	1.5	1.5
84	5.5	4.6	6.5	6.5	12.0	21.2	4.6	1.8
85	19.2	12.8	15.4	7.7	17.9	42.3	10.2	3.8
86	4.8	3.2	2.1	1.1	5.3	10.6	nd	nd
87	nd	nd	10.3	41.3	nd	36.2	20.7	15.5
88	48.3	32.2	32.2	16.1	8.1	96.7	16.1	5.4
89	56.8	56.8	56.8	39.7	90.8	249.7	39.7	17.0
90	17.4	9.8	10.9	6.5	6.5	28.2	6.5	nd
91	7.2	4.1	4.1	6.1	4.1	11.3	2.0	4.1
92	3.2	1.6	1.1	2.7	2.7	8.0	2.1	1.1
93	5.5	2.8	4.1	2.1	2.8	11.0	1.4	0.7
94	2.8	0.9	1.4	nd	2.8	5.5	nd	nd
95	nd	nd	nd	nd	nd	nd	nd	nd
96	nd	nd	nd	nd	nd	nd	nd	nd
97	nd	nd	nd	nd	nd	nd	nd	nd
98	nd	nd	nd	nd	nd	nd	nd	nd
99	nd	nd	nd	nd	nd	nd	nd	nd
100	0.8	1.2	nd	nd	1.2	1.2	0.8	0.8
101	nd	nd	nd	nd	nd	nd	nd	nd
102	2.4	0.6	1.8	0.3	3.0	1.2	0.9	0.9

S-#	PF4-11	PF4-12	PF4-13	PD4	PF5-1	PF5-2	PF5-3	PF5-4
1	174.5	18.6	7.4	17.1	18.3	nd	9.2	174.1
2	40.7	7.4	3.7	nd	13.8	nd	4.6	87.6
3	83.6	8.9	3.6	nd	20.3	5.1	12.7	96.2
4	35.7	4.6	1.8	nd	14.2	nd	3.6	60.5
5	28.1	nd	nd	nd	1.7	nd	0.3	1.7
6	1.0	nd	nd	nd	2.2	nd	nd	2.2
7	15.7	nd	nd	nd	nd	nd	nd	nd
8	8.6	3.4	10.3	nd	1.3	1.3	nd	nd
9	6.1	1.0	1.0	nd	0.8	0.4	0.2	3.2
10	7.5	1.1	1.1	nd	1.7	0.9	nd	4.4
11	13.3	1.8	1.2	nd	0.8	0.6	0.6	4.4
12	27.4	3.7	2.5	nd	1.2	1.2	1.2	6.2
13	4.2	0.8	1.1	nd	2.8	0.7	nd	5.8
14	9.2	0.5	2.8	nd	2.4	2.4	nd	6.9
15	29.5	nd	nd	nd	nd	nd	nd	nd
16	23.6	3.9	2.0	nd	nd	4.6	nd	10.8
17	14.5	nd	nd	nd	nd	nd	nd	14.0
18	15.1	nd	nd	nd	nd	nd	nd	nd
19	13.7	4.4	7.9	nd	1.0	2.0	nd	nd
20	nd	nd	nd	nd	6.8	nd	nd	17.0
21	1.6	nd	nd	nd	nd	nd	3.0	8.9
22	24.7	7.3	5.1	nd	6.3	4.2	2.1	27.2
23	24.1	4.3	1.7	nd	9.0	0.9	3.0	45.2
24	34.0	10.2	4.5	nd	12.2	1.5	3.0	45.7
25	23.3	4.1	2.9	2.9	10.2	3.4	6.8	60.9
26	30.0	4.4	nd	nd	nd	nd	1.5	11.9
27	19.7	6.6	3.6	nd	2.5	0.8	0.8	27.7
28	59.9	6.0	nd	nd	nd	nd	nd	33.9
29	18.5	1.4	nd	nd	0.7	0.7	nd	20.0
30	20.6	5.2	2.1	nd	0.5	1.4	0.5	11.6
31	7.0	nd	nd	nd	nd	nd	nd	5.2
32	21.7	2.2	nd	nd	0.5	nd	0.5	9.9
33	67.5	14.1	6.3	19.1	11.6	2.3	7.0	88.3
34	29.0	4.3	2.1	nd	5.8	nd	nd	28.2
35	22.8	3.8	2.5	nd	6.6	nd	0.8	27.1
36	27.2	8.8	5.9	nd	2.3	5.8	nd	37.3
37	7.9	2.3	1.7	nd	1.7	1.7	nd	15.0
38	17.5	2.2	2.2	nd	nd	4.7	3.1	46.6
39	16.6	4.6	4.2	nd	4.1	4.1	2.1	32.1
40	nd	nd	nd	nd	nd	0.9	nd	16.9
41	13.8	nd	nd	nd	1.3	nd	nd	14.2
42	9.4	2.0	nd	nd	1.2	12.2	1.2	31.8
43	5.2	1.5	1.9	2.6	0.7	5.8	2.2	18.7
44	2.5	0.4	0.4	13.7	4.4	1.6	1.6	10.3
45	3.9	1.0	0.7	nd	2.1	3.2	2.1	10.7
46	7.8	1.8	1.2	nd	nd	nd	1.4	18.5
47	1.7	0.6	0.3	nd	1.0	2.4	0.8	4.7
48	9.3	nd	nd	nd	1.7	nd	nd	5.2
49	15.3	2.1	nd	nd	nd	nd	nd	2.3
50	74.2	nd	nd	12.1	nd	nd	nd	3.0
51	12.0	3.8	1.5	nd	6.8	1.9	1.0	23.3
52	nd	nd	nd	nd	3.0	1.5	nd	7.5

S-#	PF4-11	PF4-12	PF4-13	PD4	PF5-1	PF5-2	PF5-3	PF5-4
53	3.0	nd	nd	nd	2.4	4.7	1.2	9.5
54	nd	nd	nd	nd	1.3	1.3	nd	5.1
55	8.1	1.1	1.1	7.4	2.4	11.2	4.0	26.3
56	2.5	0.5	0.7	4.1	1.8	2.5	0.9	6.4
57	2.9	0.6	1.5	3.3	2.7	2.4	0.5	5.3
58	11.8	2.8	1.7	nd	nd	nd	nd	20.5
59	11.8	3.4	1.3	nd	nd	nd	1.2	16.0
60	58.7	22.7	9.3	nd	nd	nd	nd	138.8
61	13.3	3.1	2.3	nd	nd	nd	nd	14.0
62	9.0	nd	nd	nd	nd	nd	nd	12.6
63	11.9	3.0	2.0	170.0	6.5	0.6	1.8	19.4
64	17.3	3.1	2.4	123.0	7.6	1.9	2.8	32.1
65	46.7	10.6	5.3	158.0	11.6	2.3	7.0	88.5
66	30.9	7.3	4.1	137.0	7.2	1.8	5.4	67.0
67	60.8	9.7	6.9	192.0	12.3	3.1	6.1	92.1
68	56.1	8.5	7.3	116.0	9.7	3.2	3.2	90.5
69	56.7	11.9	7.5	nd	nd	nd	nd	49.6
70	31.4	7.9	4.5	nd	nd	nd	2.6	38.5
71	68.5	6.5	1.6	3.1	nd	nd	3.0	52.7
72	58.5	15.4	7.7	4.5	nd	nd	nd	37.7
73	7.5	1.6	1.2	5.2	0.3	0.6	0.3	11.8
74	4.3	1.3	0.9	nd	0.5	0.5	0.2	9.9
75	4.6	1.0	0.6	nd	0.5	0.5	0.5	9.4
76	8.4	2.0	0.9	nd	nd	nd	4.9	35.7
77	13.1	2.2	1.6	nd	nd	1.8	6.3	35.9
78	8.3	0.9	0.6	nd	nd	nd	2.2	13.1
79	5.3	1.9	1.2	8.1	nd	nd	0.8	6.7
80	6.5	1.2	0.5	3.3	nd	nd	1.4	10.8
81	4.5	1.6	0.5	5.1	nd	nd	1.1	8.1
82	12.2	2.3	1.5	2.5	nd	nd	2.7	28.7
83	19.5	4.9	3.9	4.4	nd	nd	2.3	33.7
84	29.5	4.6	2.8	10.9	nd	nd	0.9	36.0
85	7.7	nd	nd	3.6	nd	nd	14.2	109.0
86	nd	nd	nd	nd	nd	nd	3.2	30.7
87	222.1	20.7	10.3	nd	nd	nd	37.4	358.6
88	5.4	nd	nd	nd	nd	nd	24.7	185.3
89	28.4	11.4	nd	nd	nd	nd	35.9	344.3
90	30.4	6.5	3.3	nd	4.8	2.4	19.3	103.9
91	10.2	4.1	2.0	nd	nd	nd	2.3	21.5
92	9.6	2.1	1.6	nd	nd	nd	3.8	23.6
93	11.0	2.8	2.1	nd	nd	nd	5.7	30.0
94	5.5	nd	nd	nd	3.4	1.1	3.4	16.5
95	nd	nd	nd	nd	nd	nd	1.4	7.2
96	nd	nd	nd	nd	nd	1.8	nd	5.3
97	nd	nd	nd	nd	nd	nd	0.5	3.8
98	nd	nd	nd	nd	2.6	0.9	nd	6.0
99	nd	nd	nd	nd	nd	nd	nd	nd
100	1.6	0.4	0.4	nd	nd	nd	0.5	4.6
101	nd	nd	nd	nd	nd	nd	nd	4.4
102	3.0	1.2	0.6	5.6	nd	nd	3.1	10.7

S-#	PF5-5	PF5-6	PF5-7	PF5-8	PF5-9	PF5-10	PF5-11	PF5-12
1	45.8	128.3	82.5	128.3	45.8	82.5	146.6	119.1
2	23.1	78.4	32.3	27.7	18.4	32.3	55.3	87.6
3	25.3	70.9	53.2	68.4	25.3	45.6	76.0	78.5
4	21.4	57.0	32.0	24.9	14.2	28.5	39.2	64.1
5	0.7	1.4	1.7	2.7	1.0	0.5	3.4	2.0
6	nd	1.7	0.2	0.2	nd	nd	1.7	1.7
7	nd	0.5	1.6	1.6	0.3	0.3	3.8	1.6
8	nd	13.2	2.6	4.0	4.0	6.6	14.5	17.2
9	1.2	4.0	1.6	2.6	1.8	2.4	3.8	4.8
10	0.9	7.8	1.7	3.5	1.7	2.6	5.2	8.3
11	2.2	5.0	1.7	2.2	0.6	2.2	3.9	5.2
12	1.9	6.8	1.9	3.1	1.2	5.0	7.5	12.4
13	1.2	4.9	1.4	1.9	1.2	1.9	3.0	4.6
14	0.8	8.1	2.4	2.4	0.8	3.2	6.5	8.9
15	nd	22.6	9.0	9.0	9.0	2.3	18.0	31.6
16	9.2	24.6	12.3	9.2	15.4	7.7	18.5	26.1
17	3.5	9.4	8.2	7.0	8.2	7.0	nd	nd
18	nd	14.9	nd	nd	nd	nd	8.5	8.5
19	nd	9.4	0.5	3.0	0.5	2.0	9.9	12.8
20	6.8	25.5	10.2	20.4	10.2	10.2	23.8	34.0
21	5.9	23.7	8.9	8.9	8.9	10.4	14.8	29.7
22	10.5	21.0	11.5	9.4	8.4	13.6	23.1	31.4
23	12.1	33.2	12.1	15.1	13.6	18.1	24.1	31.7
24	16.7	36.5	18.3	18.3	18.3	21.3	33.5	44.1
25	16.9	57.5	18.6	16.9	13.5	20.3	32.1	49.1
26	3.0	13.4	6.0	11.9	3.0	6.0	22.4	25.4
27	7.5	25.0	8.3	9.2	10.0	14.2	16.7	24.2
28	6.2	43.1	6.2	18.5	6.2	18.5	46.2	52.3
29	5.2	20.7	6.7	13.3	5.9	11.8	17.8	20.0
30	2.4	8.2	5.8	6.3	2.9	5.3	7.7	10.1
31	2.1	13.6	2.1	5.2	nd	nd	10.5	15.7
32	1.6	9.4	2.6	5.7	3.1	4.7	8.9	9.9
33	20.9	69.7	27.9	23.2	23.2	34.8	46.4	60.4
34	7.8	23.3	7.8	8.7	5.8	10.7	14.6	17.5
35	6.6	20.5	7.4	7.4	6.6	9.9	11.5	14.8
36	11.7	30.3	8.2	11.7	8.2	11.7	18.7	25.7
37	5.0	18.9	5.6	6.7	3.9	6.1	9.5	16.2
38	12.4	52.8	14.0	15.5	12.4	18.6	23.3	34.2
39	8.3	nd	36.3	10.4	11.4	6.2	12.4	18.7
40	2.8	12.2	1.9	3.8	0.9	1.9	10.4	10.4
41	1.9	12.3	2.6	4.5	1.3	3.2	8.4	9.1
42	11.0	33.0	9.8	9.8	11.0	12.2	17.1	26.9
43	5.8	15.8	5.8	7.2	5.8	7.2	7.2	12.2
44	4.0	8.3	3.2	4.0	2.4	3.6	5.2	6.0
45	3.2	9.6	3.2	4.3	2.7	3.2	8.5	7.5
46	5.7	17.8	5.7	7.1	5.0	7.1	7.8	15.6
47	2.0	3.1	1.2	1.2	0.8	1.6	2.0	3.5
48	1.2	5.0	1.5	2.6	1.2	1.2	3.8	4.1
49	nd	1.0	0.4	0.4	0.4	0.4	1.9	0.8
50	1.2	3.7	0.9	7.3	0.9	0.9	6.1	1.8
51	7.8	23.3	7.8	7.8	7.8	8.8	15.6	25.3

S-#	PF5-5	PF5-6	PF5-7	PF5-8	PF5-9	PF5-10	PF5-11	PF5-12
53	2.4	8.3	2.4	4.7	1.2	2.4	4.7	4.7
54	1.3	5.1	1.3	2.5	0.6	1.3	2.5	2.5
55	6.4	19.9	4.0	4.8	3.2	6.4	8.8	12.8
56	1.4	4.6	1.8	2.3	1.4	2.3	3.6	4.1
57	1.6	5.3	1.9	1.9	1.6	2.1	3.2	3.7
58	6.3	26.0	6.3	8.7	5.5	9.4	14.2	18.9
59	6.1	19.6	6.1	7.4	4.9	8.6	11.0	16.0
60	40.5	202.3	46.3	92.5	69.4	92.5	185.0	219.7
61	5.2	28.0	7.0	7.0	5.2	8.7	14.0	19.2
62	4.9	15.4	4.9	4.2	4.2	7.0	7.0	13.3
63	4.7	17.6	5.3	5.9	4.1	5.9	8.2	11.7
64	7.6	29.3	8.5	8.5	7.6	10.4	13.2	20.8
65	23.3	72.2	21.0	28.0	21.0	28.0	37.3	58.2
66	14.5	58.0	14.5	21.7	18.1	21.7	36.2	47.1
67	27.6	116.7	24.6	24.6	18.4	30.7	36.9	73.7
68	25.9	116.4	25.9	25.9	19.4	32.3	45.3	77.6
69	15.5	49.6	18.6	26.3	18.6	27.9	31.0	40.3
70	11.6	33.4	7.7	10.3	5.1	11.6	14.1	21.8
71	15.1	55.7	16.6	16.6	13.6	19.6	21.1	31.6
72	10.8	47.2	13.5	16.2	10.8	17.5	24.3	35.0
73	3.0	12.1	3.5	4.1	3.0	4.4	5.0	6.5
74	2.0	8.1	2.0	3.0	2.0	3.2	4.4	6.4
75	2.3	8.7	2.3	3.3	1.9	3.1	3.8	5.2
76	10.5	34.0	8.1	10.5	7.3	12.2	17.8	25.9
77	11.7	32.3	9.0	9.0	7.2	11.7	12.6	25.1
78	4.4	13.8	3.6	3.3	2.2	3.6	4.4	6.6
79	1.6	4.7	1.6	2.0	1.2	1.8	2.8	3.6
80	2.9	8.6	2.3	2.9	2.0	3.4	5.1	5.7
81	1.9	6.0	1.7	2.6	1.7	2.6	3.8	4.9
82	7.3	25.3	7.3	10.7	5.3	9.3	15.3	20.0
83	6.9	16.8	7.6	7.6	6.1	9.2	10.7	16.8
84	9.0	30.6	9.0	10.8	6.3	11.7	16.2	27.0
85	33.2	66.4	33.2	42.7	28.4	42.7	4.7	9.5
86	9.7	19.4	10.5	12.1	9.7	9.7	1.6	0.8
87	119.5	298.8	119.5	89.6	74.7	112.1	14.9	14.9
88	57.7	98.8	49.4	53.5	41.2	53.5	8.2	12.4
89	129.1	301.3	129.1	114.8	86.1	129.1	21.5	43.0
90	36.2	62.8	24.2	29.0	19.3	29.0	29.0	43.5
91	7.7	15.4	6.1	6.1	4.6	5.4	6.1	10.7
92	9.6	19.8	9.6	10.2	6.4	9.6	12.8	20.4
93	13.0	22.7	8.9	9.7	8.9	12.2	15.4	25.1
94	6.9	17.1	8.0	6.3	3.4	5.7	8.0	13.7
95	2.2	3.6	2.9	2.9	2.9	2.9	2.5	5.4
96	1.3	3.5	2.6	2.6	3.5	3.5	4.4	4.4
97	2.0	2.3	nd	nd	nd	nd	2.5	2.8
98	1.7	2.6	0.9	0.9	0.4	1.7	nd	nd
99	nd	nd	nd	nd	nd	nd	nd	nd
100	1.5	2.3	0.5	1.3	0.5	1.0	1.5	1.5
101	1.3	3.8	1.9	1.3	1.3	1.6	2.2	3.1
102	4.2	6.1	3.8	3.8	2.3	3.4	3.8	6.5

S-#	PF5-13	PD5-1	PD5-2	PD5-3	PD5-4	PD5-5	PD5-6	PD5-7
1	18.3	28.6	8.6	37.2	5.7	7.2	11.4	40.1
2	13.8	58.6	9.3	40.1	4.6	12.3	9.3	18.5
3	17.7	15.1	2.7	38.3	1.4	4.1	4.1	8.2
4	12.5	41.5	8.3	20.8	4.2	8.3	8.3	14.5
5	nd	2.6	nd	1.8	nd	nd	1.3	0.9
6	nd	1.2	nd	1.5	nd	nd	nd	nd
7	0.3	nd	nd	nd	nd	nd	nd	nd
8	2.6	11.2	7.5	14.9	7.5	3.7	7.5	nd
9	0.4	2.9	1.0	2.9	0.5	0.5	0.5	1.9
10	0.9	4.2	1.4	11.2	2.8	2.8	0.8	2.8
11	1.1	nd	nd	nd	nd	nd	nd	nd
12	0.6	nd	nd	nd	nd	nd	nd	nd
13	0.5	6.0	0.8	7.6	nd	0.8	2.3	3.0
14	1.2	7.5	1.9	7.5	nd	3.8	3.8	3.8
15	4.5	3.3	nd	8.1	nd	nd	nd	nd
16	4.6	31.8	4.5	31.8	4.5	4.5	13.6	4.5
17	nd	7.4	11.1	26.0	nd	7.4	nd	nd
18	nd	6.4	nd	16.0	nd	4.8	nd	3.2
19	nd	1.3	nd	2.7	nd	nd	nd	nd
20	10.2	13.9	4.6	18.6	nd	nd	nd	nd
21	5.9	6.2	2.1	4.1	nd	nd	nd	nd
22	6.3	16.8	7.5	18.6	5.6	5.6	7.5	9.3
23	3.0	15.3	6.8	17.0	5.1	3.4	6.8	8.5
24	7.6	23.9	10.2	20.5	3.4	3.4	10.2	13.6
25	6.8	42.2	7.5	30.1	4.5	9.0	7.5	15.1
26	1.5	8.0	3.4	9.1	nd	nd	4.5	6.8
27	4.2	15.6	6.2	9.4	4.7	6.2	6.2	10.9
28	6.2	12.2	nd	18.4	18.4	18.4	12.2	24.5
29	2.2	6.1	1.2	6.1	1.2	2.4	2.4	6.1
30	1.0	2.9	0.6	2.9	0.6	0.6	0.6	2.3
31	nd	nd	nd	nd	nd	nd	nd	nd
32	nd	2.1	nd	6.4	nd	nd	nd	1.1
33	9.3	39.6	6.6	22.0	4.4	6.6	8.8	30.8
34	2.9	16.5	8.2	13.7	5.5	5.5	8.2	16.5
35	0.8	17.2	11.5	14.3	nd	4.3	7.2	8.6
36	3.5	11.6	nd	7.7	nd	nd	3.9	3.9
37	2.2	8.1	3.2	6.5	1.6	1.6	3.2	3.2
38	6.2	29.4	8.4	15.8	3.2	6.3	11.6	14.7
39	21.8	10.3	13.7	20.6	nd	6.9	17.2	10.3
40	nd	nd	nd	nd	nd	nd	nd	nd
41	nd	nd	nd	nd	nd	nd	nd	nd
42	4.9	7.4	nd	5.9	1.5	3.0	1.5	4.4
43	1.4	2.7	0.9	5.4	0.9	0.9	0.9	2.7
44	1.6	6.3	4.2	8.5	nd	4.2	2.1	6.3
45	nd	2.2	1.1	5.6	nd	nd	nd	1.1
46	1.4	2.3	nd	6.0	1.5	1.5	1.5	0.8
47	0.8	0.7	nd	4.4	nd	0.7	nd	0.7
48	nd	1.3	nd	0.6	nd	nd	nd	nd
49	nd	nd	nd	nd	nd	nd	nd	nd
50	nd	1.3	nd	2.7	nd	nd	nd	2.7
51	3.9	4.7	1.2	3.0	nd	nd	nd	3.0
52	1.5	4.2	1.0	3.1	nd	1.0	2.1	1.6

S-#	PF5-13	PD5-1	PD5-2	PD5-3	PD5-4	PD5-5	PD5-6	PD5-7
53	1.2	2.3	nd	2.3	nd	nd	1.2	1.2
54	0.6	2.6	nd	3.5	nd	nd	nd	1.7
55	nd	1.8	0.5	1.2	0.5	0.7	0.7	1.2
56	0.7	0.9	0.4	1.1	0.4	0.4	0.4	0.7
57	0.5	1.5	0.4	1.8	0.2	0.9	0.4	1.1
58	2.4	1.9	0.5	1.2	0.1	0.1	0.6	1.0
59	1.8	1.6	0.5	2.1	0.2	0.3	0.7	1.4
60	23.1	52.3	20.9	32.8	11.9	14.9	25.4	20.9
61	2.6	1.7	0.6	2.4	0.5	0.4	0.7	1.2
62	1.4	2.0	0.5	2.2	0.7	0.7	0.5	2.2
63	1.2	39.1	3.9	62.5	3.9	23.5	3.9	31.3
64	1.9	44.9	7.5	74.9	7.5	18.7	7.5	30.0
65	4.7	55.2	7.4	103.1	7.4	22.1	11.0	36.8
66	3.6	40.9	5.8	70.2	5.8	20.5	8.8	29.2
67	9.2	72.2	7.6	117.8	7.6	30.4	7.6	38.0
68	9.7	46.1	4.2	62.9	4.2	16.8	8.4	21.0
69	4.6	5.3	0.7	4.4	0.5	1.5	1.9	3.1
70	1.3	5.1	1.1	4.4	0.4	1.1	1.1	2.9
71	4.5	8.3	2.4	8.9	2.1	2.4	3.0	4.7
72	4.0	14.9	9.3	7.5	3.7	7.9	6.5	3.3
73	0.9	7.9	2.0	4.5	1.6	2.4	2.4	4.5
74	0.7	6.0	1.4	4.3	0.7	2.1	2.1	4.3
75	0.5	4.5	1.1	2.9	0.5	1.3	1.2	2.5
76	4.1	5.0	1.2	3.4	0.6	1.5	1.5	2.6
77	3.6	3.5	0.5	3.1	0.4	1.1	1.1	2.7
78	1.5	2.0	0.3	0.9	0.1	0.4	0.2	0.6
79	0.2	1.4	0.3	0.8	0.3	0.3	0.9	nd
80	0.9	1.2	0.1	0.6	0.1	0.2	0.2	0.9
81	0.6	2.0	0.5	1.1	0.2	0.4	0.5	1.0
82	2.0	7.8	3.1	3.1	1.2	1.9	3.7	2.3
83	2.3	8.7	2.5	5.3	1.3	2.1	2.5	3.8
84	3.6	6.4	1.9	2.6	0.6	1.5	1.9	1.9
85	7.1	68.8	1.8	38.8	10.6	21.2	nd	21.2
86	2.4	7.4	nd	4.6	nd	2.8	nd	2.8
87	29.9	166.6	nd	98.5	7.6	37.9	nd	30.3
88	8.2	67.5	nd	40.9	8.2	20.4	nd	22.5
89	35.9	160.1	7.6	91.5	15.2	38.1	nd	49.6
90	9.7	18.7	4.4	13.2	4.4	5.5	5.5	8.8
91	2.3	8.8	3.1	3.1	1.3	0.9	1.8	3.5
92	5.1	7.9	2.2	6.5	2.2	2.7	3.8	4.9
93	6.5	7.0	1.4	3.2	1.8	0.7	2.5	3.5
94	4.6	8.5	0.8	5.4	1.2	2.3	0.8	5.4
95	nd	3.4	nd	nd	nd	nd	nd	nd
96	nd	nd	nd	nd	nd	nd	nd	nd
97	nd	nd	nd	nd	nd	nd	nd	nd
98	nd	nd	nd	nd	nd	nd	nd	nd
99	nd	nd	nd	nd	nd	nd	nd	nd
100	nd	0.8	nd	1.3	nd	0.6	nd	0.4
101	0.3	1.4	0.3	1.2	nd	nd	0.2	1.4
102	1.5	2.1	0.3	2.4	1.1	0.9	1.5	1.7

S-#	PD5-8	PD5-9	PD5-10	PF6-1	PF6-2	PF6-3	PF6-4	PF6-5
1	10.0	4.3	2.9	5.5	77.4	243.1	22.1	33.2
2	6.2	3.1	3.1	3.7	59.2	177.6	14.8	22.2
3	2.7	1.4	nd	6.1	42.8	143.8	12.2	30.6
4	4.2	nd	nd	5.8	23.3	46.7	7.8	19.4
5	nd	nd	nd	nd	0.6	2.7	nd	1.3
6	nd	nd	nd	nd	nd	3.0	nd	2.0
7	nd	nd	nd	nd	nd	nd	nd	nd
8	nd	nd	nd	nd	nd	7.8	nd	nd
9	1.0	1.0	0.5	0.6	1.2	5.8	0.6	4.0
10	2.8	0.8	nd	nd	2.9	19.8	1.5	7.3
11	nd	nd	nd	nd	2.6	12.4	0.5	7.9
12	nd	nd	nd	1.1	2.3	22.7	4.5	7.9
13	nd	nd	nd	nd	3.9	23.2	1.1	7.7
14	1.9	nd	nd	1.8	4.4	26.6	1.8	16.0
15	nd	nd	nd	nd	nd	nd	nd	17.7
16	nd	nd	nd	nd	8.5	36.2	2.1	14.9
17	nd	nd	nd	nd	nd	37.8	4.2	14.7
18	nd	nd	nd	nd	nd	19.5	6.5	13.0
19	nd	nd	nd	nd	nd	4.2	nd	1.4
20	nd	nd	nd	nd	nd	27.3	nd	23.9
21	nd	nd	nd	nd	nd	nd	nd	18.2
22	7.5	1.9	3.7	nd	4.2	20.9	2.1	5.2
23	1.7	1.7	nd	3.4	20.6	68.8	10.3	10.3
24	3.4	1.7	1.7	3.1	18.9	53.5	6.3	12.6
25	4.5	3.0	1.5	2.8	51.3	131.1	8.5	11.4
26	nd	nd	nd	nd	nd	13.3	nd	5.7
27	4.7	1.6	nd	nd	8.8	42.9	4.9	5.9
28	nd	nd	nd	nd	nd	38.3	nd	7.7
29	1.2	nd	nd	nd	10.6	36.1	2.6	7.0
30	nd	nd	nd	nd	6.0	24.8	3.4	4.0
31	nd	nd	nd	nd	3.0	19.7	nd	nd
32	nd	nd	nd	nd	6.9	20.1	nd	1.9
33	6.6	4.4	2.2	1.5	21.2	69.5	7.6	7.6
34	8.2	2.7	nd	1.7	11.7	33.5	5.0	5.9
35	4.3	1.4	nd	1.6	8.9	35.6	3.2	6.5
36	1.9	nd	nd	nd	8.4	34.3	5.6	11.1
37	1.6	1.6	1.6	nd	7.0	23.2	2.9	5.8
38	6.3	4.2	2.1	nd	21.5	71.2	8.3	9.9
39	10.3	6.9	3.4	3.7	23.9	82.9	7.4	36.8
40	nd	nd	nd	nd	13.5	29.9	1.9	2.9
41	nd	nd	nd	nd	8.5	22.0	nd	0.7
42	1.5	1.5	nd	3.4	41.1	140.3	13.7	20.5
43	0.9	nd	nd	1.3	15.8	47.4	5.3	10.5
44	nd	nd	nd	2.0	8.0	24.5	3.3	6.0
45	nd	nd	nd	1.7	6.7	20.8	2.5	5.0
46	0.8	nd	nd	nd	18.9	54.1	1.4	9.5
47	nd	nd	nd	1.0	3.5	9.6	1.0	1.9
48	nd	nd	nd	nd	0.7	9.8	nd	1.6
49	nd	nd	nd	nd	nd	9.4	nd	nd
50	1.3	nd	nd	0.9	1.7	4.9	0.6	2.3
51	nd	nd	nd	nd	7.5	27.6	0.7	9.0
52	nd	nd	nd	0.4	4.2	12.2	0.4	5.3

S-#	PD5-8	PD5-9	PD5-10	PF6-1	PF6-2	PF6-3	PF6-4	PF6-5
53	nd	nd	nd	0.9	1.4	10.4	0.9	1.8
54	nd	nd	nd	0.6	3.5	8.9	0.6	4.5
55	0.5	nd	nd	1.3	17.3	61.1	5.3	9.3
56	0.2	nd	nd	0.2	2.5	9.9	0.5	2.5
57	0.4	nd	nd	1.2	3.5	11.0	0.9	2.9
58	0.6	0.2	0.2	nd	20.6	66.3	4.4	11.8
59	0.5	nd	nd	0.9	10.6	38.1	2.7	8.9
60	17.9	9.0	6.0	nd	83.0	272.7	23.7	47.4
61	0.4	0.1	0.1	1.0	14.4	45.2	3.1	10.3
62	0.4	0.4	0.2	1.0	11.9	39.7	5.0	9.9
63	3.9	nd	nd	0.9	11.2	35.4	1.7	6.1
64	7.5	3.7	3.7	1.3	15.4	55.3	5.1	6.4
65	11.0	3.7	2.2	nd	31.6	145.4	12.6	12.6
66	8.8	2.9	nd	nd	32.8	140.9	13.1	13.1
67	7.6	3.8	2.3	2.1	56.9	163.6	17.8	14.2
68	6.3	2.1	2.1	1.8	32.9	131.8	12.0	15.0
69	1.5	1.0	0.5	nd	6.8	34.2	4.3	8.5
70	0.7	nd	nd	nd	11.0	38.4	2.7	5.5
71	2.1	1.2	0.9	0.8	11.2	36.8	4.0	6.4
72	2.3	nd	nd	nd	8.0	35.4	3.2	7.2
73	2.6	1.0	0.4	0.4	4.2	16.0	1.9	4.2
74	2.4	0.7	0.7	0.5	6.1	19.5	1.9	3.7
75	1.5	0.5	0.4	0.3	5.4	14.2	0.7	2.4
76	1.0	0.4	nd	3.0	25.6	67.9	4.5	7.5
77	0.5	0.5	0.4	1.3	17.8	53.4	2.5	7.6
78	nd	nd	nd	0.8	7.3	17.0	1.2	1.6
79	nd	nd	nd	0.2	2.8	8.3	0.5	3.2
80	0.2	nd	nd	1.6	5.6	16.8	1.6	5.6
81	0.4	0.2	0.1	1.1	4.7	12.1	1.1	2.6
82	2.1	1.0	0.8	2.6	12.9	37.8	2.6	6.9
83	1.7	0.6	0.4	2.3	8.0	25.2	2.3	8.0
84	0.8	0.4	nd	1.9	9.3	38.2	2.8	9.3
85	24.7	nd	nd	nd	23.3	83.4	7.8	23.3
86	1.4	nd	nd	nd	11.4	40.9	3.8	8.6
87	nd	15.1	nd	nd	115.0	253.0	23.0	23.0
88	22.5	nd	nd	nd	37.7	115.7	10.8	21.5
89	22.9	nd	nd	nd	65.2	183.5	16.3	24.5
90	4.4	2.2	1.1	7.3	39.2	105.3	14.7	19.6
91	1.8	1.8	nd	3.5	16.1	41.5	6.9	9.2
92	1.6	1.1	nd	2.3	16.6	48.9	7.0	9.3
93	1.4	nd	nd	1.5	17.5	55.5	8.8	10.2
94	nd	nd	nd	0.9	14.1	30.8	3.5	5.3
95	nd	nd	nd	nd	6.1	15.6	nd	4.5
96	nd	nd	nd	nd	4.3	14.0	nd	4.3
97	nd	nd	nd	nd	3.2	8.0	0.6	1.6
98	nd	nd	nd	nd	1.5	9.2	1.5	3.8
99	nd	nd	nd	nd	nd	nd	nd	nd
100	nd	nd	nd	nd	2.3	7.7	0.6	1.1
101	nd	nd	nd	nd	3.0	9.0	0.4	1.5
102	0.6	nd	nd	0.4	6.9	14.6	0.9	2.6

S-#	PF6-6	PF6-7	PF6-8	PF6-9	PF6-10	PF6-11	PF6-12	PD6-1
1	270.7	187.9	44.2	27.6	187.9	33.2	77.4	101.9
2	122.1	88.8	33.3	22.2	140.6	7.4	37.0	128.8
3	143.8	82.6	30.6	30.6	128.5	18.4	49.0	74.7
4	52.5	38.9	19.4	9.7	85.5	5.8	31.1	64.6
5	2.9	3.1	nd	nd	5.4	1.5	2.3	4.2
6	1.2	1.0	nd	nd	2.7	nd	0.2	3.6
7	1.5	1.7	nd	0.4	3.8	0.4	1.7	5.6
8	nd	nd	nd	nd	18.3	1.3	5.2	13.6
9	4.0	2.6	1.4	1.2	7.5	0.9	1.7	9.8
10	14.7	10.3	2.9	2.9	22.0	1.5	4.4	15.6
11	7.9	6.2	4.4	3.5	14.1	nd	nd	8.2
12	13.6	9.1	2.3	4.5	22.7	3.4	7.9	13.6
13	7.2	5.5	1.1	1.1	11.6	1.1	1.7	13.7
14	5.3	7.1	3.5	3.5	31.9	1.8	5.3	26.2
15	17.7	11.8	17.7	17.7	70.6	nd	nd	59.2
16	49.0	38.4	23.4	12.8	49.0	4.3	21.3	33.0
17	21.0	16.8	21.0	4.2	27.3	nd	nd	25.9
18	16.2	13.0	9.7	3.2	25.9	nd	nd	39.8
19	5.6	1.4	3.5	1.4	22.6	1.4	5.6	66.5
20	44.4	27.3	41.0	nd	nd	nd	nd	86.0
21	52.4	11.4	nd	nd	nd	nd	nd	79.3
22	13.6	11.5	5.2	4.2	35.5	4.2	8.4	55.7
23	49.9	37.8	10.3	6.9	51.6	1.7	10.3	68.8
24	37.8	28.3	12.6	11.0	58.3	6.3	14.2	83.2
25	96.9	57.0	17.1	11.4	68.4	2.8	14.2	62.1
26	16.2	11.4	3.8	nd	28.5	nd	7.6	51.6
27	33.2	21.5	6.8	3.9	21.5	1.0	7.8	47.4
28	53.6	19.2	nd	7.7	88.1	nd	34.5	86.4
29	24.7	18.5	4.4	3.5	17.6	1.8	6.2	21.2
30	14.8	10.7	2.7	2.7	12.1	0.7	4.7	21.6
31	16.6	13.6	nd	nd	14.4	nd	1.5	22.8
32	15.7	9.4	3.1	0.6	15.0	nd	3.8	22.2
33	51.4	33.3	10.6	6.0	40.8	3.0	10.6	42.2
34	21.8	15.9	5.0	3.4	16.8	3.4	10.1	49.4
35	17.8	12.9	4.8	3.2	14.5	1.6	7.3	43.1
36	24.1	18.6	9.3	7.4	25.1	0.9	10.2	45.3
37	25.0	15.1	5.2	3.5	17.4	2.3	4.6	42.7
38	57.9	39.7	9.9	6.6	38.1	3.3	11.6	92.1
39	44.2	31.3	9.2	9.2	29.5	3.7	9.2	232.5
40	19.3	16.4	2.9	1.0	15.4	nd	1.9	40.0
41	23.4	8.5	0.7	0.7	9.9	nd	1.4	28.6
42	75.3	54.7	17.1	20.5	68.4	3.4	20.5	50.6
43	29.0	22.4	7.9	3.9	27.6	1.3	10.5	37.8
44	11.9	7.3	3.3	1.3	11.9	0.7	2.7	42.7
45	15.0	10.0	3.3	4.2	12.5	0.8	1.7	41.2
46	24.4	20.3	4.1	1.4	18.9	nd	4.1	24.6
47	5.7	3.8	1.6	0.6	4.8	0.6	1.3	8.4
48	5.5	5.2	0.7	nd	6.5	0.3	4.2	6.7
49	6.0	6.0	nd	nd	6.9	nd	1.7	1.7
50	6.3	8.0	0.9	0.6	8.6	5.7	6.9	3.6
51	15.7	11.9	6.0	3.7	23.1	0.7	9.0	31.7
52	5.3	5.0	0.8	0.4	5.7	0.4	2.3	38.1

S-#	PF6-6	PF6-7	PF6-8	PF6-9	PF6-10	PF6-11	PF6-12	PD6-1
53	6.3	3.2	0.9	nd	5.0	nd	2.7	5.1
54	3.5	3.2	0.6	0.6	4.5	0.6	1.3	5.0
55	19.9	18.6	4.0	2.7	15.9	1.3	5.3	18.3
56	3.5	2.5	0.5	0.5	3.2	0.5	1.0	9.4
57	4.0	2.9	1.4	0.9	4.0	nd	1.4	10.7
58	30.9	26.5	5.9	2.9	20.6	1.5	4.4	34.6
59	21.3	15.1	2.7	1.8	17.7	0.9	4.4	44.9
60	183.8	130.4	35.6	23.7	142.3	5.9	35.6	327.1
61	38.0	24.7	6.2	4.1	30.8	2.1	6.2	28.6
62	17.9	11.9	4.0	3.0	11.9	2.0	9.9	34.4
63	14.7	10.4	1.7	1.7	13.8	0.9	3.5	50.4
64	28.3	18.0	3.9	2.6	23.2	1.3	5.1	54.8
65	82.2	60.1	12.6	6.3	56.9	3.2	9.5	84.8
66	85.2	59.0	13.1	6.6	59.0	3.3	13.1	86.6
67	110.2	60.5	21.3	14.2	74.7	7.1	21.3	79.0
68	83.9	56.9	18.0	12.0	71.9	6.0	18.0	85.1
69	25.6	18.8	4.3	3.4	17.1	0.9	5.1	35.3
70	22.9	17.4	4.6	1.8	16.5	1.8	5.5	27.8
71	25.6	17.6	4.0	2.4	12.8	1.6	4.8	27.2
72	26.6	17.7	4.8	4.0	19.3	1.6	4.0	68.0
73	9.5	7.6	1.5	1.1	6.5	0.4	1.5	24.6
74	10.7	6.5	1.9	1.4	7.4	0.5	1.9	23.4
75	6.8	4.7	1.0	0.7	4.1	0.7	1.4	13.4
76	33.2	24.1	4.5	3.0	25.6	0.9	6.0	14.5
77	22.9	16.5	3.8	1.3	22.9	nd	5.1	12.0
78	12.1	6.5	2.0	0.8	8.9	0.4	2.4	4.0
79	3.9	3.2	0.7	0.5	3.7	0.1	1.8	4.6
80	7.2	5.6	1.2	0.8	7.2	0.2	1.6	5.1
81	5.8	4.2	0.8	0.8	5.3	0.3	1.1	8.6
82	22.4	17.2	4.3	2.6	18.9	1.7	5.2	38.6
83	11.4	8.6	2.9	2.9	18.9	0.6	3.4	37.7
84	24.2	17.7	5.6	3.7	29.8	0.9	7.5	35.1
85	46.6	34.9	11.6	7.8	13.6	nd	7.8	136.7
86	24.7	19.0	3.8	1.9	1.0	1.0	1.9	9.7
87	184.0	115.0	34.5	11.5	23.0	5.8	17.3	49.0
88	59.2	43.1	10.8	8.1	8.1	2.7	5.4	66.7
89	118.2	81.5	32.6	16.3	48.9	2.4	24.5	70.3
90	49.0	41.6	12.2	7.3	26.9	1.5	7.3	47.8
91	19.6	13.8	4.6	2.3	11.5	nd	nd	28.2
92	27.9	23.3	5.8	3.5	14.0	1.2	2.3	34.3
93	38.0	29.2	8.8	5.8	24.8	nd	2.9	23.0
94	20.2	15.8	5.3	3.5	16.7	0.9	3.5	13.2
95	10.6	6.7	nd	nd	6.7	nd	nd	6.7
96	8.6	5.4	2.2	1.1	6.5	nd	nd	4.5
97	4.5	2.2	nd	nd	2.5	nd	nd	5.3
98	4.6	3.5	2.3	1.5	3.8	nd	nd	2.8
99	nd	nd	nd	nd	nd	nd	nd	nd
100	4.6	3.4	0.6	0.6	2.9	0.3	0.6	2.1
101	5.2	4.9	0.7	0.7	5.2	0.7	1.5	5.4
102	9.4	7.7	1.3	0.9	5.6	0.4	1.7	8.1

S-#	PD6-2	PD6-3	PD6-4	PD6-5	PD6-6	PD6-7	PF7-1	PF7-2
1	84.9	163.0	27.2	88.3	81.5	61.1	187.6	11.7
2	202.4	230.0	27.6	46.0	64.4	59.8	138.6	11.6
3	90.7	122.7	16.0	32.0	42.7	37.3	148.8	9.5
4	83.0	101.5	11.5	23.1	32.3	30.0	57.8	5.3
5	4.2	9.0	1.2	8.4	6.0	3.6	5.2	nd
6	3.2	7.0	nd	1.1	2.9	1.6	2.3	nd
7	2.1	9.1	1.4	5.9	5.9	5.2	0.8	nd
8	20.4	37.4	3.4	6.8	6.8	nd	11.4	nd
9	6.9	16.6	1.5	3.9	4.9	3.4	5.4	0.4
10	31.3	26.1	4.3	8.7	12.2	7.8	17.6	0.9
11	10.9	12.7	1.8	5.4	7.3	4.5	9.6	1.9
12	9.9	22.2	3.7	12.4	9.9	7.4	17.6	1.1
13	15.8	24.7	2.7	5.5	8.2	4.8	28.4	2.1
14	25.0	42.9	3.6	11.9	17.9	9.5	23.0	1.0
15	16.9	93.0	16.9	16.9	25.4	29.6	18.9	nd
16	79.2	69.3	6.6	19.8	19.8	13.2	34.7	6.2
17	18.2	46.7	13.0	23.3	23.3	28.5	16.3	6.5
18	23.9	39.8	4.0	31.8	21.9	19.9	18.1	6.0
19	20.8	83.1	16.6	12.5	18.7	20.8	4.8	1.6
20	68.8	103.2	51.6	43.0	43.0	51.6	24.2	4.8
21	55.5	79.3	39.7	23.8	39.7	47.6	28.8	10.1
22	24.7	82.5	12.4	14.4	24.7	20.6	34.8	4.5
23	63.5	105.8	21.2	26.4	37.0	42.3	51.1	6.4
24	58.2	105.4	19.4	19.4	36.1	33.3	61.1	10.2
25	124.2	91.8	10.8	18.9	27.0	24.3	167.1	17.8
26	21.7	103.3	13.6	19.0	29.9	29.9	14.0	1.2
27	28.1	62.2	7.4	14.8	20.7	16.3	39.9	4.8
28	66.1	116.9	10.2	20.3	25.4	50.8	17.5	nd
29	22.1	30.6	2.8	11.1	11.1	11.1	32.1	4.0
30	17.5	37.0	3.1	8.2	10.3	10.3	27.2	3.4
31	18.3	41.1	nd	4.6	10.7	4.6	30.4	1.8
32	14.8	36.0	1.1	11.6	12.7	11.6	23.2	1.4
33	74.3	74.3	8.4	20.3	23.6	27.0	73.3	6.5
34	25.4	55.1	8.5	18.4	14.1	14.1	51.5	5.2
35	28.7	64.7	8.6	14.4	17.2	17.2	36.1	2.5
36	45.3	60.5	15.1	15.1	18.5	20.2	19.7	nd
37	39.7	67.1	9.2	15.3	19.8	18.3	22.6	2.1
38	78.2	128.4	22.3	30.7	39.1	39.1	56.9	5.2
39	132.8	390.2	49.8	66.4	124.5	99.6	86.9	4.7
40	30.4	40.0	nd	3.8	15.2	7.6	34.2	nd
41	25.4	47.7	3.2	4.8	22.3	19.1	34.2	nd
42	80.4	89.3	35.7	41.7	41.7	44.7	127.1	15.9
43	37.8	75.5	15.5	17.8	24.4	22.2	35.7	3.2
44	26.3	59.1	16.4	16.4	19.7	16.4	21.8	2.6
45	24.7	61.8	4.1	18.5	28.8	26.8	27.6	1.8
46	36.3	37.6	13.0	7.8	20.7	13.0	57.3	12.1
47	8.0	8.4	2.7	1.9	5.3	4.6	14.5	2.6
48	6.2	9.8	nd	1.8	6.2	2.2	15.7	nd
49	nd	7.8	nd	8.3	8.9	nd	14.5	nd
50	2.7	8.2	nd	12.7	8.2	8.2	15.4	nd
51	17.6	70.5	10.6	14.1	26.4	21.1	34.6	1.3
52	13.3	83.7	9.5	13.3	30.4	26.6	22.8	1.0

S-#	PD6-2	PD6-3	PD6-4	PD6-5	PD6-6	PD6-7	PF7-1	PF7-2
53	0.9	7.7	nd	3.8	3.8	1.7	11.7	nd
54	3.6	7.9	nd	4.3	5.0	2.5	16.8	nd
55	13.7	27.4	6.5	6.5	10.4	6.5	42.4	5.5
56	5.8	14.9	2.2	2.9	4.3	2.9	10.0	1.0
57	6.4	16.2	2.1	4.3	5.1	4.3	14.2	2.0
58	23.8	47.5	8.6	10.8	14.0	8.6	50.7	5.8
59	21.1	60.7	7.9	10.6	17.2	10.6	42.3	5.5
60	218.0	523.3	43.6	87.2	163.5	87.2	154.3	25.7
61	30.5	41.9	6.7	9.5	13.3	10.5	90.7	10.1
62	23.6	40.8	8.6	14.0	12.9	10.7	26.9	5.7
63	64.6	69.3	7.9	18.9	22.1	18.9	55.4	5.0
64	71.3	76.8	9.1	18.3	25.6	20.1	84.1	9.8
65	113.0	135.0	12.6	31.4	43.9	31.4	175.3	23.9
66	98.9	142.2	18.6	37.1	49.5	37.1	182.9	24.9
67	124.1	129.8	16.9	33.9	45.1	28.2	274.8	42.7
68	93.6	127.7	14.2	28.4	39.7	28.4	205.4	26.8
69	24.7	51.8	11.8	11.8	16.5	14.1	56.6	6.4
70	21.8	41.7	9.9	9.9	12.9	11.9	67.1	10.7
71	23.4	44.8	13.6	9.7	14.6	11.7	63.5	8.3
72	32.4	74.5	22.7	13.0	21.1	19.4	47.3	3.5
73	14.1	36.9	3.5	8.8	12.3	8.8	30.9	4.8
74	19.9	37.3	4.3	10.4	13.0	8.7	32.1	3.6
75	12.4	19.6	1.9	5.3	6.7	4.8	21.3	2.5
76	22.9	24.7	3.0	6.0	8.4	6.0	84.1	9.8
77	10.7	22.7	2.5	5.7	8.2	5.7	83.4	7.6
78	6.3	6.3	0.7	1.1	1.8	1.4	42.6	4.6
79	4.9	8.4	0.9	1.9	3.5	2.3	14.0	0.9
80	3.7	8.3	0.9	2.1	3.7	1.9	31.0	1.6
81	9.8	13.5	1.8	2.5	3.7	3.4	18.0	1.6
82	23.4	63.4	6.9	8.3	20.7	13.8	36.0	4.0
83	29.6	61.9	6.7	10.8	18.8	13.5	17.4	1.2
84	23.4	49.2	7.0	8.2	16.4	11.7	31.6	2.4
85	106.8	179.4	21.4	59.8	76.9	34.2	48.7	4.4
86	23.7	12.5	1.4	7.0	10.4	2.8	31.9	3.2
87	179.8	69.5	8.2	24.5	32.7	12.3	167.3	15.6
88	66.7	90.5	14.3	38.1	47.6	19.1	85.5	9.9
89	110.9	113.6	16.2	32.5	43.3	16.2	122.1	14.5
90	39.1	91.2	26.1	15.2	30.4	15.2	113.8	27.1
91	16.9	45.2	16.9	8.5	16.9	11.3	63.6	17.9
92	21.6	48.3	15.3	10.2	15.3	14.0	56.2	16.0
93	20.7	39.0	10.3	11.5	16.1	11.5	89.0	25.4
94	37.4	28.6	11.0	5.5	8.8	6.6	55.1	12.4
95	15.9	14.6	3.1	3.7	3.7	1.2	42.6	6.4
96	8.9	9.8	1.8	1.8	3.6	2.7	32.1	4.0
97	2.7	5.3	nd	nd	nd	nd	20.0	2.8
98	1.7	4.0	1.1	3.4	2.8	2.0	25.3	5.9
99	nd	nd	nd	nd	nd	nd	20.1	nd
100	3.2	4.8	0.8	1.6	2.9	0.8	19.3	2.7
101	7.9	9.2	2.1	2.1	3.8	3.3	20.7	2.4
102	9.2	15.3	4.6	3.1	6.1	4.1	32.3	6.5

S-#	PF7-3	PF7-4	PD7-1	PD7-2	PF8	PD8	VAPTOT	PARTTOT
1	78.2	62.5	306.9	392.1	130.0	874	750	5434
2	92.4	40.4	480.1	677.9	64.4	1426	1677	5171
3	101.3	63.3	302.4	434.6	82.4	982	1814	4158
4	46.0	21.0	290.1	398.9	40.3	591	655	2733
5	3.6	2.4	22.4	39.6	14.9	83	227	282
6	3.0	0.5	29.9	39.9	1.1	80	264	199
7	2.0	1.8	34.0	55.3	8.2	110	127	287
8	17.2	nd	102.3	113.7	20.3	160	569	724
9	7.2	1.8	59.6	64.4	4.7	140	450	417
10	14.1	4.4	57.4	69.6	11.4	221	958	681
11	12.1	5.1	55.2	71.8	13.8	189	1797	528
12	19.8	7.7	99.5	119.5	33.0	232	1164	814
13	22.8	4.3	121.3	131.7	14.4	270	2276	805
14	28.8	5.8	258.3	281.7	24.9	293	1663	1276
15	48.6	nd	194.2	254.8	38.9	464	671	1626
16	19.9	14.9	108.4	150.6	26.9	241	1082	1416
17	29.3	9.8	138.4	145.6	32.1	286	578	1157
18	24.2	6.0	118.6	142.4	29.5	270	464	1024
19	11.9	3.6	185.0	185.0	8.2	335	333	1104
20	26.6	7.2	246.9	258.1	21.2	402	542	1821
21	28.8	11.5	258.0	258.0	32.4	264	717	1497
22	23.6	9.0	293.2	398.8	23.5	348	789	1869
23	30.7	12.8	247.1	312.9	22.7	693	2386	2415
24	40.7	17.0	431.3	496.7	29.6	748	2968	2999
25	49.8	21.3	199.4	243.7	49.8	608	1733	2714
26	14.0	4.3	224.3	270.7	10.2	490	301	1586
27	20.9	5.7	184.7	238.3	11.5	531	308	1695
28	16.2	nd	217.8	278.2	7.0	484	416	2076
29	11.2	3.2	61.8	83.2	12.4	212	434	858
30	10.9	5.4	73.2	93.8	12.1	258	524	821
31	10.1	nd	63.2	81.8	19.5	243	478	682
32	12.7	3.5	90.7	122.3	9.6	310	273	861
33	44.0	16.3	221.9	305.1	31.3	601	131	2634
34	25.8	9.0	126.4	171.6	33.2	352	144	1408
35	27.1	6.6	173.8	249.2	14.7	528	119	1620
36	29.5	9.0	188.7	231.3	16.4	652	184	1823
37	13.1	4.7	131.9	145.1	13.2	431	142	1242
38	31.0	12.9	308.6	315.4	37.0	982	289	2858
39	103.3	14.1	1404.1	1499.9	67.6	5107	2336	10007
40	19.5	4.9	158.8	188.2	4.5	519	527	1233
41	21.7	4.6	226.7	233.3	7.0	606	421	1438
42	57.2	15.9	199.0	231.0	46.7	615	1777	2428
43	31.5	11.6	191.2	246.8	18.9	608	1266	1708
44	17.3	5.1	215.5	215.5	17.7	670	801	1565
45	18.4	2.8	196.1	206.9	31.0	651	807	1510
46	27.1	10.5	136.7	154.3	28.9	488	1547	1370
47	6.8	2.6	32.3	37.0	17.4	141	307	371
48	11.7	6.7	46.3	62.7	9.3	177	814	440
49	10.9	1.0	7.2	52.9	20.6	327	671	517
50	13.5	8.7	33.1	53.8	31.0	366	703	753
51	50.6	9.3	793.5	1396.5	24.7	3020	2629	5847
52	43.4	5.2	559.7	990.3	26.0	3400	2348	5358

S-#	PF7-3	PF7-4	PD7-1	PD7-2	PF8	PD8	VAPTOT	PARTTOT
53	15.2	2.3	48.8	79.2	15.6	431	708	733
54	24.5	2.6	54.1	91.9	25.7	811	718	1120
55	18.4	2.8	129.7	151.3	32.0	684	1758	1476
56	7.1	1.0	120.0	139.0	10.0	729	1174	1142
57	10.5	2.0	125.5	135.5	18.7	790	1162	1244
58	19.6	3.5	209.5	189.5	49.0	926	559	1962
59	16.5	2.8	257.3	228.7	45.0	1010	836	2050
60	77.1	12.9	1263.6	1516.4	204.0	6530	4069	13684
61	24.2	6.0	296.2	261.8	84.6	1020	1232	2287
62	12.8	1.4	177.7	163.3	36.7	598	398	1426
63	21.4	5.0	252.7	270.3	42.7	890	1125	2426
64	31.3	9.8	347.6	323.4	57.0	1040	1059	2937
65	47.8	15.9	342.5	358.5	123.0	1140	2817	4177
66	41.6	16.6	466.0	455.0	124.0	1910	839	4947
67	61.1	24.4	374.2	382.8	237.0	1000	723	4685
68	67.0	26.8	446.4	466.6	114.0	1040	689	4268
69	38.6	10.3	393.4	421.6	31.0	1270	668	2998
70	34.6	10.7	331.1	413.9	40.5	1160	611	2628
71	29.0	8.3	228.4	285.6	49.0	964	225	2433
72	33.1	4.7	434.8	445.2	21.2	946	338	2775
73	15.1	3.4	153.0	176.0	21.1	492	147	1175
74	14.6	3.6	169.8	182.2	22.5	510	292	1202
75	10.4	2.0	98.2	102.8	13.5	298	303	736
76	29.3	7.8	138.1	148.9	35.4	564	1450	1527
77	30.3	5.7	133.9	146.1	39.3	451	3263	1365
78	14.8	5.6	45.7	51.1	38.7	243	1329	625
79	19.6	3.3	69.2	93.8	16.8	459	1480	787
80	32.6	3.1	78.6	106.4	28.1	581	1998	1018
81	11.5	2.5	96.5	94.5	18.5	528	800	913
82	24.0	6.4	197.9	229.1	19.3	375	854	1405
83	24.9	4.6	391.0	465.0	10.1	902	1022	2302
84	28.5	9.5	265.0	278.0	14.6	521	846	1749
85	62.0	11.8	1225.7	1114.3	21.2	2370	1186	6460
86	23.9	4.8	158.8	167.2	12.7	521	940	1267
87	77.8	23.3	414.4	395.6	32.4	840	1707	5150
88	67.6	13.9	727.7	782.3	40.8	1920	1608	5370
89	64.0	20.4	504.7	492.3	36.3	926	1392	5633
90	54.2	10.8	489.2	570.8	137.0	1850	1230	4470
91	35.9	6.5	386.1	408.9	60.8	1230	1267	2662
92	34.8	8.0	390.9	433.1	68.5	1380	498	2912
93	36.0	8.5	234.8	256.2	87.9	669	503	1970
94	23.4	5.5	136.7	156.3	64.5	444	734	1272
95	14.9	3.2	160.6	120.4	32.8	542	547	1059
96	18.1	4.0	122.5	122.5	41.0	517	859	973
97	11.1	1.7	83.9	95.1	25.4	339	584	628
98	18.6	2.5	104.0	128.0	38.0	629	1414	1018
99	11.1	nd	112.8	90.2	31.9	718	1169	984
100	8.6	2.7	53.5	62.5	29.6	429	616	675
101	13.0	2.4	135.1	151.9	26.2	723	593	1166
102	13.7	3.2	127.5	147.5	46.0	721	448	1281